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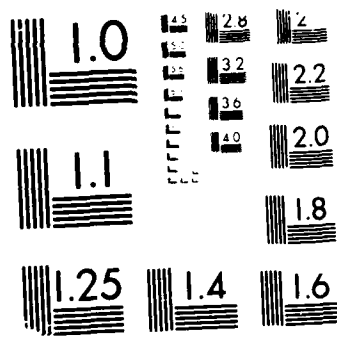
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MASSACHUSETTS INSTITUTE OF TECHNOLOGY

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PROPULSION ALTERNATIVES FOR AN UNDERSEA  
AUTONOMOUS VEHICLE

by

John Leonard Braun

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PROPULSION ALTERNATIVES FOR AN UNDERSEA  
AUTONOMOUS VEHICLE

by

John Leonard Braun

B.S., United States Naval Academy  
(1981)

SUBMITTED TO THE OCEAN ENGINEERING DEPARTMENT  
IN PARTIAL FULFILLMENT OF THE REQUIREMENTS  
FOR THE DEGREES OF

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and

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at the

MASSACHUSETTS INSTITUTE OF TECHNOLOGY, June 1987

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PROPULSION ALTERNATIVES FOR AN UNDERSEA  
AUTONOMOUS VEHICLE

by

John Leonard Braun

Submitted to the Department of Ocean Engineering on 8 May 1987  
in partial fulfillment of the requirements for the degrees of  
Naval Engineer and Master of Science in Mechanical Engineering

ABSTRACT

A study was conducted to determine suitable energy systems for small undersea autonomous vehicles. The two main goals of this study were: (1) to evaluate energy systems which would be able to provide 16 kW-hr for a vehicle of specified dimensions, and; (2) to evaluate energy systems which may be used in the future for longer duration, higher speed missions. It was concluded that silver-zinc secondary batteries are satisfactory for the low energy requirement.

There is some uncertainty about the most suitable energy source for the higher energy mission. There are no fully developed systems which are completely safe, reliable, and readily available for use. Lithium thionyl chloride batteries, and lithium sulfurhexafluoride thermal power plants are the main contenders and have comparable energy densities. There are concerns, however, about the safety and availability of each of these systems.

Thesis Supervisor: A. Douglas Carmichael  
Title: Professor of Power Engineering



## ACKNOWLEDGEMENTS

This thesis, the culmination of a year-long effort, carries the name of but one author. Even so, it represents the contributions of many people who deserve recognition here.

First of all, I would like to thank all of the professionals whose names appear in Appendix B, for without their help, this work would not have been possible. I would also like to thank my thesis advisor, Professor Carmichael, whose patience and guidance was invaluable.

My office-mates, the other two Amigos, deserve thanks as well. The levity they injected, in the form of pick-up basketball games and lunchtime "schmooz" sessions, helped to keep me sane during the past year. The love, support, and encouragement of the extended Braun and Peters families is also deserving of recognition.

I reserve the lion's share of my gratitude, however, for the two special ladies in my life. My daughter Meghan is a joy; she is more than any first-time father could hope for. My wife Mary has been extremely supportive and understanding during the last three years. As we approach our third anniversary, I am only just beginning to appreciate how lucky I really am.

Cambridge, Massachusetts

May 8, 1987



## TABLE OF CONTENTS

ABSTRACT . . . . .	2
ACKNOWLEDGEMENTS . . . . .	3
TABLE OF CONTENTS . . . . .	4
LIST OF FIGURES . . . . .	6
LIST OF TABLES . . . . .	7
 Chapter 1: BACKGROUND . . . . .	 8
 Chapter 2: SILVER-ZINC BATTERIES	
2.1 INTRODUCTION . . . . .	13
2.2 TECHNICAL DESCRIPTION . . . . .	15
2.3 SAFETY . . . . .	17
2.4 INSTALLATION DETAILS . . . . .	19
2.5 CURRENT ASSESSMENT . . . . .	27
 Chapter 3: LITHIUM THIONYL CHLORIDE BATTERIES	
3.1 INTRODUCTION . . . . .	29
3.2 TECHNICAL DESCRIPTION . . . . .	30
3.3 SAFETY . . . . .	31
3.4 INSTALLATION DETAILS . . . . .	34
3.5 CURRENT ASSESSMENT . . . . .	39
 Chapter 4: SODIUM-SULFUR BATTERIES	
4.1 INTRODUCTION . . . . .	45
4.2 TECHNICAL DESCRIPTION . . . . .	45
4.3 SAFETY . . . . .	54
4.4 INSTALLATION DETAILS . . . . .	58
4.5 CURRENT ASSESSMENT . . . . .	58



## TABLE OF CONTENTS (CONT D)

### Chapter 5: FUEL CELLS

5.1 INTRODUCTION . . . . .	60
5.2 TECHNICAL DESCRIPTION . . . . .	61
5.3 SAFETY . . . . .	63
5.4 INSTALLATION DETAILS . . . . .	65
5.5 CURRENT ASSESSMENT . . . . .	65

### Chapter 6: OTHER SYSTEMS

6.1 INTRODUCTION . . . . .	69
6.2 LITHIUM SULFURHEXAFLUORIDE THERMAL POWER PLANTS. .	69
6.3 RADIOACTIVE ISOTOPE SYSTEMS . . . . .	70

### Chapter 7: CONCLUSIONS AND RECOMMENDATIONS

7.1 INTRODUCTION . . . . .	74
7.2 CONCLUSIONS . . . . .	74
7.3 RECOMMENDATIONS . . . . .	76

REFERENCES . . . . .	78
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### APPENDICES:

A. DESCRIPTION OF A TYPICAL SILVER-ZINC DEEP SEA BATTERY . . . . .	81
B. INDUSTRY CONTACTS . . . . .	85



## LIST OF FIGURES

<u>Figure No.</u>	<u>Title</u>	<u>Page No.</u>
1.1	Present and Future Power Sources for Undersea Autonomous Vehicles	10
1.2	Specific Power vs Specific Energy for Batteries	11
2.1	Cut-away View of a Rechargeable Cell	16
2.2	Cell Reactions During Overcharge	20
2.3	LR-190 & L4/22 Installation	24
3.1	ALTUS HEDB Disk Stack	35
3.2	ALTUS HEDB Disk Cell & Battery Containment System	38
3.3	ALTUS HEDB Cell Installation	40
3.4	ALTUS Battery Monitoring System Block Diagram	44
4.1	Beta alumina/Beta" alumina Crystalline Structure	47
4.2	The Dow Cell	50
4.3	The Plate Cell	51
4.4	The Central Sodium Cell with Sodium Wick	52
4.5	The Central Sodium Cell with Sodium Reservoir	53
4.6	The Central Sulfur Cell	55
5.1	Representative Fuel Cell and Reactions	62
6.1	STM4-120 Stirling Engine	71
6.2	Organic Rankine Cycle (ORC) for DIPS	72
6.3	Pu-238 ORCEPS	73
A.1	Typical Deep Submergence Silver-Zinc Battery	84



## LIST OF TABLES

<u>Table No.</u>	<u>Title</u>	<u>Page No.</u>
1-1	Specific Undersea Autonomous Vehicle Requirements	9
2-1	Marketed Low-Rate Ag-Zn Cells Performance Characteristics	18
2-2	YARDNEY Low-Rate Ag-Zn Cell	21
2-3	YARDNEY Low-Rate Ag-Zn Module	22
2-4	Factors Influencing Ag-Zn Battery Life	25
3-1	ALTUS HEDB Cell Dimensions	36
3-2	ALTUS HEDB Performance Characteristics	37
4-1	Cell Type Comparison	56
5-1	Fuel Cell Types and Their Applications	64
5-2	"ORBITER" Fuel Cell Characteristics	66
5-3	Reactant Weights and Volumes	67
7-1	Energy System Summary	75



## Chapter 1

### BACKGROUND

Small, unmanned, underwater vehicles are currently being used to perform a wide range of tasks in the world's oceans. Normally, control information and power are fed to the vehicle through a tether, which restricts the vehicle's range and maneuverability. There have been recent developments in controls, navigation, and artificial intelligence (AI); however, the lack of a safe, compact, and reliable high energy power source continues to prevent the operation of untethered vehicles for long duration or high speed missions.

Early studies [1,2,3] have narrowed the field of suitable energy sources for small, autonomous undersea vehicles (Figs. 1.1 & 1.2). The purposes of this study are two-fold: (1) to consider the immediate problem of providing a 16 kW-hr energy source for initial development of small undersea vehicles, and; (2) to consider the technical and safety features of higher energy density systems for future vehicle missions of longer duration. The specific requirements of the vehicle to be considered in this study are contained in Table 1-1.

The next four chapters will cover silver-zinc batteries, lithium thionyl chloride batteries, sodium-sulfur batteries, and fuel cells. Each chapter will follow a format which: (1) introduces the energy system and gives its current applications; (2) gives a technical description of its



TABLE 1-1

SPECIFIC UNDERSEA AUTONOMOUS VEHICLE REQUIREMENTS

\* Low energy vehicle specifications:

- 16 kW-hr
- Energy compartment: 17 inch inside diameter  
21 inch outside diameter  
51 inch length

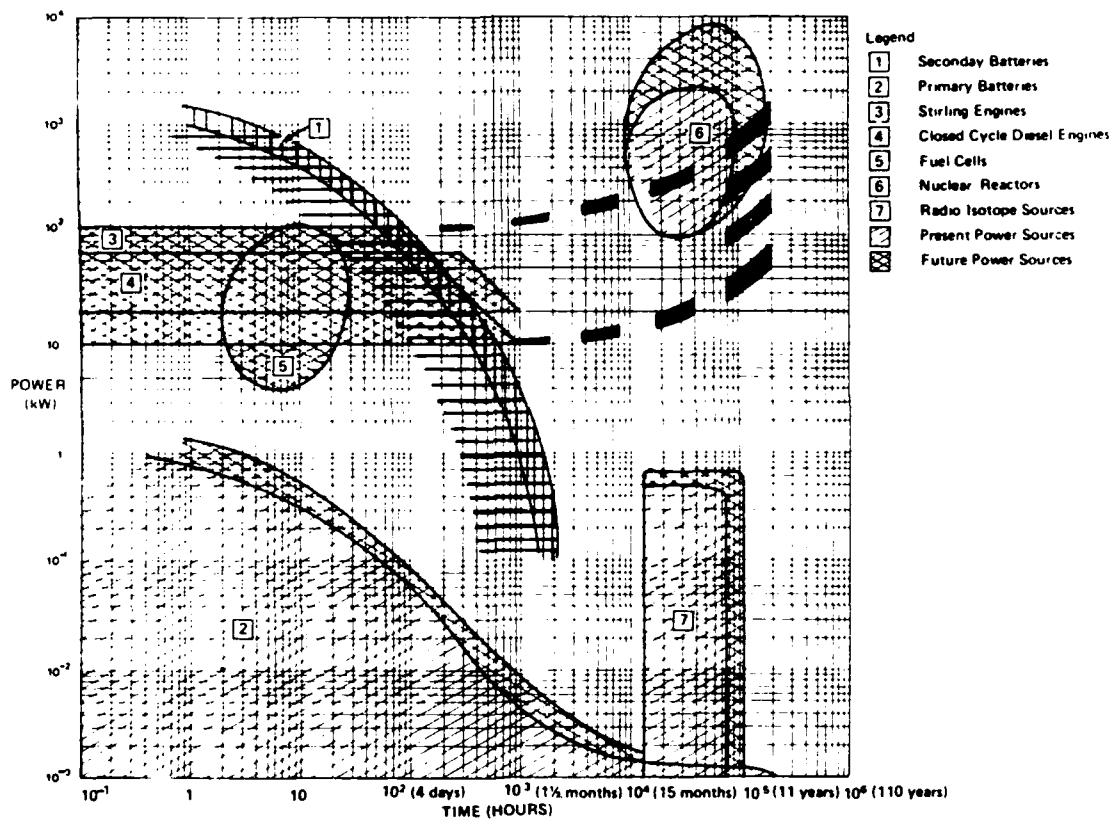
\* High energy vehicle specifications:

- 200 kW-hr
- Energy compartment: 25 inch inside diameter  
30 inch outside diameter  
51(+) inch length

\* Energy source must be safe and reliable during handling and usage in marine environment

\* Two year time frame for development, focusing on off-the-shelf technology as much as possible for the low energy application. Five to ten years is the time frame for the high energy application.





Present and Future Power Sources for Undersea Autonomous Vehicles

Figure 1.1



# Specific Power vs Specific Energy for Batteries

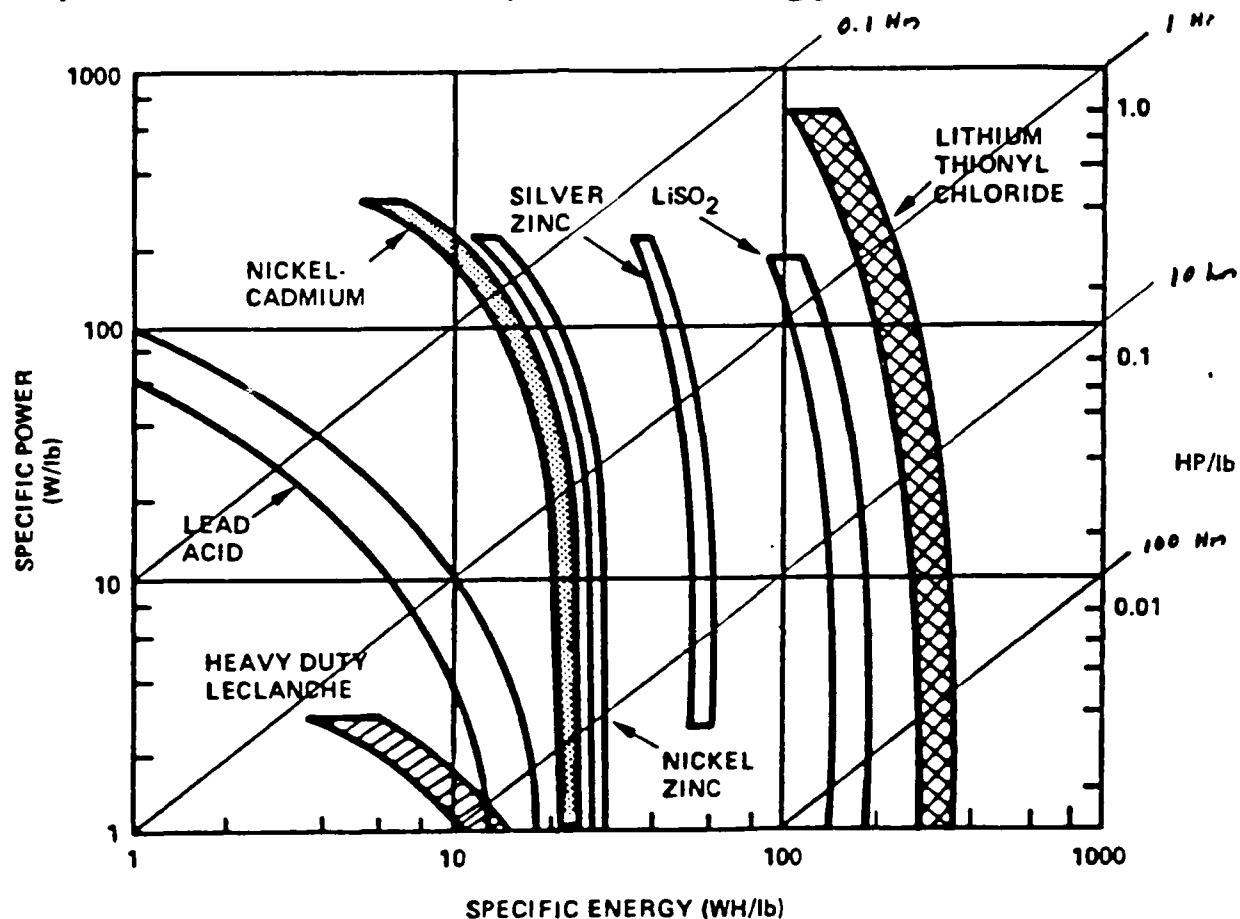


Figure 1.2



operation; (3) discusses the relevant safety concerns; (4) describes the details necessary for installation, and; (5) gives an overall assessment of that energy system as applied to the undersea vehicle described in Table 1-1.

Chapter 6 will be devoted to covering other energy systems with high energy densities which appear attractive for application in the longer duration undersea vehicle missions described earlier. Because of their obvious need for further development, these other systems will not be covered in the same detail as batteries and fuel cells. These systems include a radioactive isotope system (Pu-238), as well as the lithium sulfurhexafluoride combustor combined with either a closed cycle Brayton engine, a Stirling engine, or an organic Rankine cycle. The works of both Labak and Sydnor [4,5] have already discussed the lithium sulfurhexafluoride-Brayton system and its application in a vehicle very similar to the one described in Table 1-1.



## Chapter 2

### SILVER-ZINC BATTERIES

#### 2.1 INTRODUCTION

Though their energy density is not as high as some candidate power systems to be discussed, silver-zinc batteries are the most feasible for the undersea vehicle application described in Chapter 1, particularly for the low energy vehicle, for two main reasons. First, silver-zinc batteries have a relatively long and proven history of use, especially in undersea vehicles. By comparison, other candidate energy systems are in their infancy. Because silver-zinc batteries have worked beyond the "growing pains" stage, they could easily be installed in a developmental vehicle while further testing is done on a higher energy density source, which could then be used in longer duration mission vehicles. Second, with the calibration and test runs that will be required of this developmental vehicle, an easily rechargeable energy source would be the most advantageous.

The history of the silver-zinc cell begins in 1883 when the first primary cell was patented, followed in 1887 by the proposal of a secondary cell. These cells were mainly experimental, however, and it is doubtful that any were actually manufactured or used. The first practical rechargeable silver-zinc battery was not achieved until the publication in 1911 of Henri Andre's study of the Ag-Zn couple, when the solubility of the silver species in alkaline



electrolyte and its migration to the zinc electrode was noted. Other results of his study which eventually lead to the first rechargeable silver-zinc cell were: (1) A discovery of the semi-permeable membrane characteristics of cellophane. (2) Development of a method of controlling both the volume of the zinc compartment, as well as the pressure on the element. When used, cellophane retarded the migration of soluble silver oxides to the negative plate. Additionally, it impeded the formation of zinc dendrites between the negative and positive plates. Thus, the use of cellophane allowed the two major causes of cell short circuits to be controlled.

From this point, military applications during the infancy of silver-zinc batteries helped to hasten their transition to everyday applications. Today, they are found not only in military and aircraft applications, but also in portable industrial and photographic equipment, medical and portable electronics, and space exploration applications [7].

The attractive features of the silver-zinc battery include:

- High or low power discharge rate cells available, with good shelf-life for both types.
- Provides high currents with nearly constant voltage over discharge cycle.
- Very efficient and mechanically rugged, operating in a wide temperature range.
- Five times the mass and volume energy density of either lead-acid or nickel-zinc.

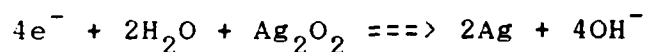


Silver-zinc cells are relatively expensive when compared to these other secondary cells, however. Other drawbacks include their sensitivity to overcharge, and shorter cycle life. Recent developments have produced a cell capable of achieving 200 cycles over 30 months, however.

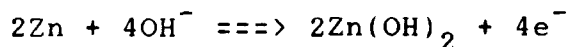
## 2.2 TECHNICAL DESCRIPTION

The discharging silver-zinc internal cell reactions are shown below:

Positive Electrode:

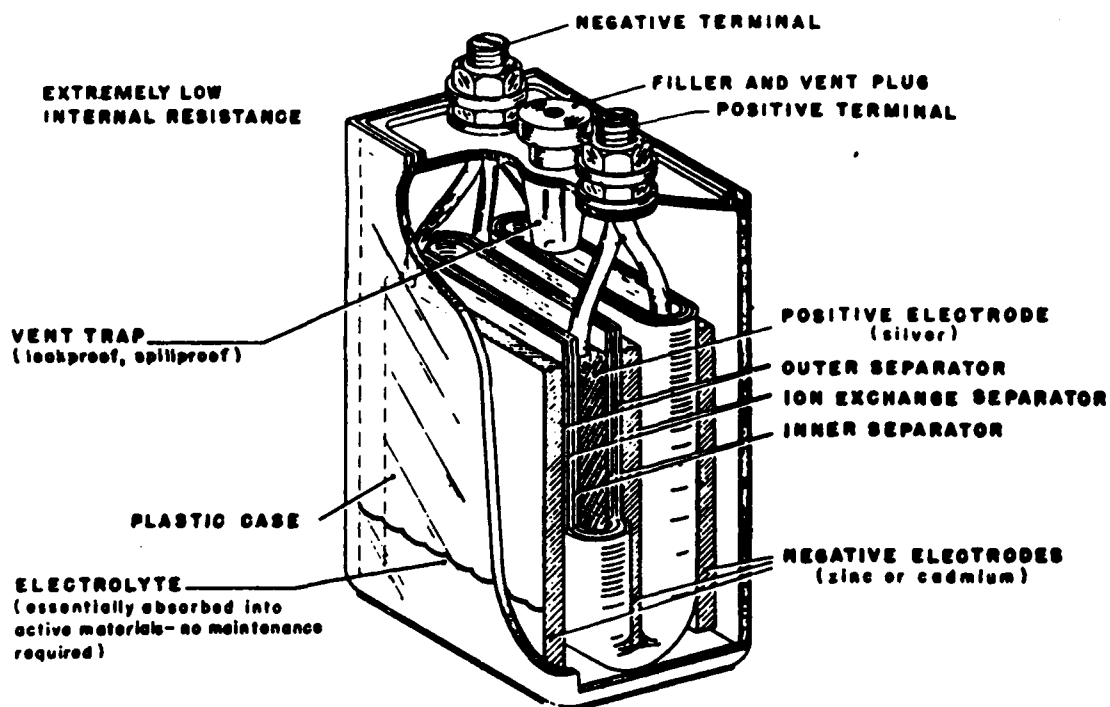


Negative Electrode:



The cut-away view of a standard, manufactured cell is shown in Figure 2.1 with all its key parts. The negative electrode is manufactured from zinc by dry pressing, by a paste method, or by electrodeposition, while the positive electrode is rolled and sintered from silver powder, with silver collectors or grids, and silver leads. The separators consist of semi-permeable and ion-exchange materials used in multiple layers around the electrodes. The electrolyte is a strong potassium hydroxide solution which is very caustic and corrosive. The cell is filled with electrolyte through the vent plug opening. Once in place, the vent plug itself performs the dual task of allowing built up gas to escape, while at the same time limiting electrolyte carry-out by the gas and limiting air entering the cell. Surrounding the cell





CUT-AWAY VIEW OF A RECHARGEABLE CELL

Figure 2.1



parts and containing the electrolyte is the cell case, which is molded in one of a variety of durable plastics [7].

Standard models exist in the 0.1-600 A-hr range and are available in a variety of standard configurations. Specially designed cells can meet almost any geometry, however. When battery containment vessels are required, they can be formed from either fiberglass, stainless steel, magnesium, or titanium, depending on environmental and/or mechanical stress design requirements. General performance characteristics for marketed low rate Ag-Zn cells are contained in Table 2-1.

### 2.3 SAFETY

Because of their long proven history, silver-zinc cell safety is well understood. For this reason, maintenance procedures exist which, if followed, will prevent any serious safety problems from occurring. Examples of cell abuse which can lead to problems are: overcharging, exposure to high temperature, discharging to complete exhaustion, or high rate short circuiting. The two main safety problems which may arise with silver-zinc cells are gas evolution and internal shorts.

Non-toxic gas production is the result of normal usage and charging. Most often the gas is hydrogen, which requires the same spark and flame safety precautions as in the lead-acid cell. Hydrogen concentrations above 8% could lead to explosion, so ventilation of the battery compartment must be addressed. The most vigorous gassing occurs when a cell is



TABLE 2-1

MARKETED LOW-RATE Ag-Zn CELLS  
PERFORMANCE CHARACTERISTICS

Energy output:

W-hr/lb	40-50
W-hr/in <sup>3</sup>	2.5-3.2
Open circuit voltage	1.82-1.86
Load voltage (nominal)	1.5
Voltage regulation (fixed load, $\pm 10^{\circ}\text{F}$ )	2%
Operating temperature range (optimum performance)	-10 to 165 <sup>o</sup> F 50 to 125 <sup>o</sup> F
Storage temperature range	wet: -55 to 100 <sup>o</sup> F dry: -85 to 165 <sup>o</sup> F
Dry storage life	up to 5 years
Wet shelf life - normal (varies w/ temp & charge)	1 to 2 years
Resistance to mechanical stress	MIL-E-527 2A
Operating attitude	any position except inverted (upright is optimum)

The following depend on cell model design and usage:

Cycle life	80-100 cycles
Internal resistance	very low
Charging time	10-20 hours



reversed. Cell reactions for both silver and zinc limited cells, showing gas production during overcharge, are shown in Figure 2.2 [7].

Internal shorts are the result of low impedance connections between the cell's positive and negative plates. They can vary from a mild short, to one in which the heating action at the short is vigorous enough to boil the electrolyte. These vigorous shorts, known as hot shorts, are rare in today's silver-zinc cells. The short itself is the result of zinc dendrites bridging plates across a separator, particularly if the cell is overcharged extensively or repeatedly [8]. Bridging through the separator can occur with separator deterioration due to oxidation, from either the soluble silver species in the electrolyte, or exposure to the air above the electrolyte. The separator can also react with the electrolyte itself, slowly forming large, potassium oxalate crystals which stress the separator [7].

#### 2.4 INSTALLATION DETAILS

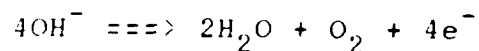
Characteristics of an available silver-zinc cell and module, manufactured by the Yardney Corporation, are shown in Tables 2-2 and 2-3 respectively. These two examples would provide the 16 kW-hr requirements of the undersea vehicle described in Chapter 1, despite the fact that some space is wasted because of the rectilinear cell design. Possible arrangements of these cells in a cylindrical space 17 inches in diameter and 51 inches long for an underwater vehicle are



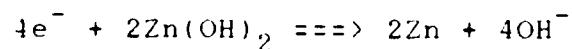
### CELL REACTIONS DURING OVERCHARGE

#### Silver limited cell:

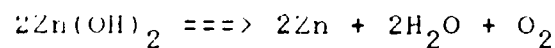
Positive electrode:



Negative electrode:

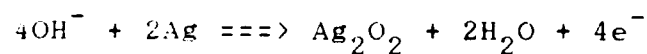


Overall cell reaction:

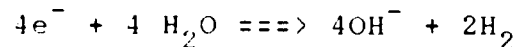


#### Zinc limited cell:

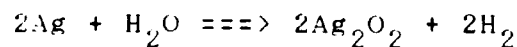
Positive electrode:



Negative electrode:

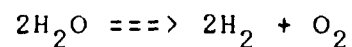


Overall cell reaction:



#### Continued overcharge:

Overall cell reaction:



### GAS EVOLVED DURING OVERCHARGE

Silver limited	12.72 in <sup>3</sup> /A-hr O <sub>2</sub> @ STP
Zinc limited	25.45 in <sup>3</sup> /A-hr H <sub>2</sub>
Overcharged	38.17 in <sup>3</sup> /A-hr O <sub>2</sub> & H <sub>2</sub>

Figure 2.2



TABLE 2-2

YARDNEY LOW-RATE Ag-Zn CELL

MODEL NUMBER LR-190:

ELECTRICAL CHARACTERISTICS:

nominal capacity (A-hrs)	190
charging rate (Amps)	8

APPLICATION DATA (@70°F):

10-hour rate discharge:

discharge (Amps)	19
A-hr output *	187
avg voltage	1.49
W-hr/lb *	63.1
W-hr/in <sup>3</sup> *	4.7

60-min rate discharge:

discharge (Amps)	190
A-hr output *	160
avg voltage	1.36

PHYSICAL CHARACTERISTICS:

maximum weight filled (oz)	70.7
overall volume (in <sup>3</sup> )	59.7
overall height (in)	6.40
width (in)	6.01
depth (in)	1.55
terminal threads	5/16-24

\* To a final voltage of 1.1 volts



TABLE 2-3

YARDNEY LOW-RATE Ag-Zn MODULE

MODULE NUMBER LR4/22:

ELECTRICAL CHARACTERISTICS:

nominal capacity (A-hrs)	22
charging rate (Amps)	1 <sup>a</sup>

APPLICATION DATA (@70°F):

10-hour rate discharge:

discharge rate (Amps)	2
A-hr output	24 <sup>b</sup>
avg voltage	6

60-min rate discharge:

discharge rate (Amps)	22
A-hr output	20 <sup>b</sup>
avg voltage	5.6

PHYSICAL CHARACTERISTICS:

maximum weight filled (oz)	41.6
overall volume (in <sup>3</sup> )	36
overall height (in)	4.33
width (in)	2.80
depth (in)	3.04
terminals	1/4-28

NOTES: a. charge to 7.90-8.00 volts/module  
b. To a final voltage of 4.4 volts



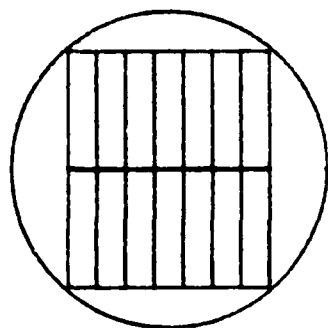
shown in Figure 2.3. This figure indicates that between 20 and 31 kW-hr of energy could be stored using existing silver-zinc batteries.

Even before installation, however, there are many factors to be considered. These include handling and storage considerations, as well as factors affecting battery life. The latter are shown in Table 2-4. Other considerations include: electrolyte filling, cell storage, capacity draining and capacity loss, and short detection. These are discussed in the following paragraphs. Still other considerations (the use of insulated tools around the battery compartment to prevent shorts, or the handling of potassium-hydroxide electrolyte with care) are common sense.

It is not uncommon for cells to experience swelling upon filling with electrolyte. For this reason, it is recommended that the filling should occur after the cells are installed in the battery container. If this is not possible, the cells should be stacked side-by-side and clamped together with wood or plastic at either end. The clamp should remain in place throughout soaking and be removed only immediately prior to cell placement into the battery container.

Cells should be left unfilled if they are not to be used within a 30 day period. In the unactivated or dry condition, cells can be stored in a cool, dry area for several years. If the cell is activated and expected to see use within 60 days, it may be stored charged in a cool, dry place. Activated cells which are not expected to see use within 60





END VIEW

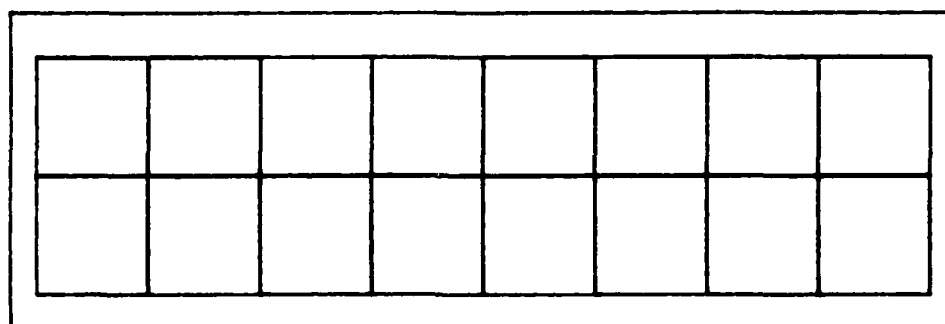
## LR-190 INSTALLATION

Total No of cells: 112

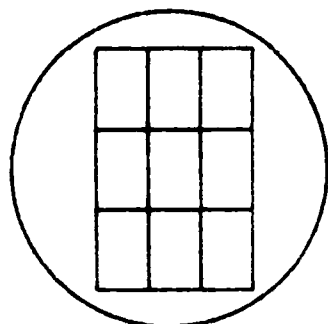
Total volume available: 11,576 cu in

Total volume used: 6,677 cu in

Total energy: 31.2 kW-hr



SIDE VIEW



END VIEW

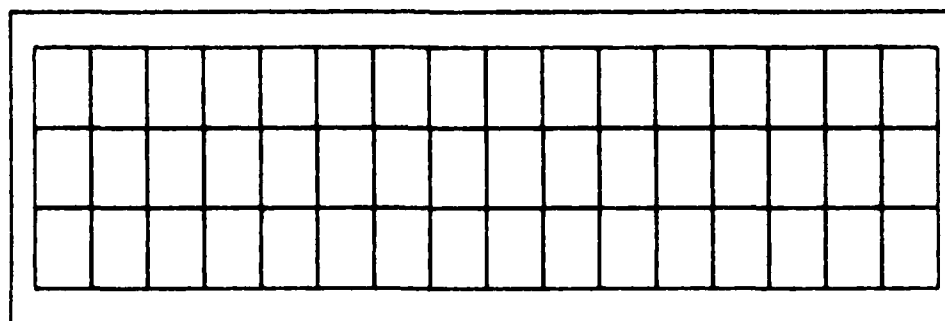
## LR4/22 INSTALLATION

Total No. of modules: 144

Total volume used: 5,307 cu in

Total energy: 20.7 kW-hr

SCALE:



SIDE VIEW

Figure 2.3



TABLE 2-4

FACTORS INFLUENCING Ag-Zn BATTERY LIFE

FACTORS WHICH TEND TO INCREASE BATTERY LIFE:

- \* Shallow capacity discharge cycling (<75%)
- \* Low current discharges (less than C rate)
- \* Moderate temperature operation (32 - 125°F)
- \* Low temperature storage (<40°F)
- \* Full charge cut-off at recommended voltage
- \* Low rate charge
- \* Regular maintenance

FACTORS WHICH TEND TO DECREASE BATTERY LIFE:

- \* Deep capacity discharge cycling (>75%)
- \* High current discharges (greater than C rate)
- \* High temperature operation (>125°F)
- \* High temperature storage (>125°F)
- \* Overcharge
- \* High rate charge (fast charge)



days should be stored in the normal discharged condition, preferably at a cold temperature (20-40°F).

As a means of ensuring the maximum number of cycles for cells assembled as a battery, it is recommended that each cell be drained of all its capacity every 10-15 cycles. Each individual cell is drained by shunting a resistor across the terminals. The resistor should be chosen to drain one-tenth the nominal hour discharge rate of current (C/10) at 1.5v, and should be removed when the cell voltage reaches 0.5v.

Eventually, a cell will lose capacity due to the inevitable degradation of cell materials with use. Occasionally, this capacity loss occurs prematurely, the result of minor abuses. In most cases, the capacity loss is reversible with a return to correct usage.

If a cell has insufficient electrolyte, it will experience poor charge acceptance, the result being a lowered capacity. If the electrolyte is extremely low, the cell could suffer permanent damage, making the capacity loss irreversible.

Low temperature operations also reduce a cell's capacity. Discharging and charging below room temperature (60-80°F) results in a loss of capacity which is fully recovered when the cell's temperature is returned to normal.

Silver-zinc cells discharged below the 40 hr rate may not accept a normal recharge. This capacity loss is usually recovered by recharging at a rate comparable to the discharge rate.



A capacity imbalance can occur in a battery due to the fact that charge efficiency is a function of temperature. Since cells toward the center of the battery have poorer heat transfer than cells toward the outside, those few internal cells may limit the capacity of the battery as a whole. This is normally corrected by maintenance procedures.

Additional causes of capacity loss can be found in cases of gross battery abuse, such as extreme shock and vibration, or unusually high temperatures. These are infrequent and obvious enough not to warrant any further discussion.

A final consideration is short detection, the key to which is cell voltage readings. To detect a short early, battery voltage monitoring equipment is required. Immediately after full charge, open cell voltage must read 1.85v; anything less is an indication of a short. During charging, cells normally plateau at 1.6v & 1.9v. Between plateaus, it is normal for cell voltage to peak and fall off. If the cell voltage continues to fall for 60 minutes, the cell is shorting [7].

## 2.5 CURRENT ASSESSMENT

The silver-zinc cell, particularly at Yardney Corporation, has had much experience in undersea applications (e.g. TRIESTE and ALVIN). Some excerpts from a Yardney Corporation publication on silver-zinc deep sea applications are contained in Appendix A [9].



As was shown in Figure 2.3, existing silver-zinc cells would only be acceptable for the low energy, initial development vehicle described in Chapter 1, and could provide between 20 and 30 kW-hr of energy storage. Because that vehicle would undoubtedly be subjected to numerous testing runs, it is obvious that the rechargeability of silver-zinc cells would prove to be an asset. Additionally, such cells are readily available with a proven safety record. A value for the silver-zinc energy density using the Yardney LR-190 and taking into account wasted volume (Fig.2.3) is 2.7 W-hr/in<sup>3</sup> and 63 W-hr/lb.

If cost ever replaces energy density as the driving consideration in a specific undersea vehicle design, nickel-zinc might be considered. Nickel-zinc cells, aside from a reduced energy density, enjoy all the advantages of the silver-zinc cell, but at a much lower price [10].



## Chapter 3

### LITHIUM THIONYL CHLORIDE BATTERIES

#### 3.1 INTRODUCTION

The lithium thionyl chloride battery is an attractive, high energy density primary battery. It boasts the following desirable features:

- Energy density greater than 200 W-hr/lb or 34.5 kW-hr/ft<sup>3</sup>
- Low cost materials that are readily available in sufficient quantities
- All materials reduce to environmentally "clean" substances
- Can operate in a wide temperature range (-4 to 212°F)
- A 10 year active shelf-life; indefinite inactive shelf-life
- Voltage stability over 95% of discharge cycle
- Less than 10% voltage change with a fixed load
- Low cell resistance for high energy utilization
- Enough versatility to provide a high or low rate, large or small capacity, in either an active or reserve cell

As with any new high energy system, there is a risk. In the case of lithium thionyl chloride batteries, several explosions have resulted from their use. The problem of safety has impeded the rapid and widespread practical application of this battery's technology [11].

There is an ample history of good performance in small cell applications. Early solid and inorganic electrolyte

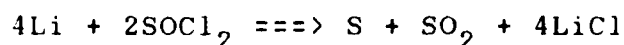


lithium cell types, up to and including the AA, C, & D sizes, have proven to be reliable over the past 10 years, in applications ranging from cardiac pacemaker implants, to standby power sources for long service-life computer memories. While these lithium cells have worked well in small sizes, it became clear that, in order to realize the benefits of high energy and compactness, larger thionyl chloride cells would have to be manufactured. These batteries could be used for undersea applications, particularly remote vehicles, sonobuoys, mines, targets, torpedoes, and swimmer delivery vehicles. Recent work has concentrated not only on making larger cells more reliable, but also understanding failure mechanisms enough to correct or avoid them [14].

Current applications of lithium thionyl chloride batteries include, radio and laser range finder power sources, and ongoing research for undersea vehicle applications is being conducted at the Naval Ocean Systems Center (NOSC) in San Diego. A possible future application is in the area of remote undersea vehicles for the petroleum industry [12,17].

### 3.2 TECHNICAL DESCRIPTION

The governing cell reaction is:



There are possible variations in electrolyte (e.g.  $\text{SOCl}_2/\text{LiAlCl}_4$  or  $\text{SOCl}_2/\text{Li}_2\text{O}:\text{AlCl}_3$ ), and a host of secondary



reactions are possible, some of which are not fully understood [16]. This is the source of some of the problems surrounding the lithium thionyl chloride cell.

Energy densities range from 140-240 W-hr/lb and approximately 28 kW-hr/ft<sup>3</sup>. Larger cells can weigh anywhere from 8 - 33 lbs with volumes from 80 - 500 in<sup>3</sup>. It is because lithium has the highest potential among metals that the lithium thionyl chloride cell has a high voltage. It also enjoys a long active shelf life --- approximately 10 years [11,12,13].

### 3.3 SAFETY

There are several areas of concern with regard to the safety of lithium thionyl chloride cells. Most concerns arise as a direct result of the volatile materials which comprise the cell. The most common result of a cell mishap or malfunction is a rapid rise in cell temperature, causing overpressure. This, in turn, results in an explosion. It is no wonder then, that safety concerns seem to increase exponentially as this very high energy cell grows in size.

Most often, a rapid rise in cell temperature is the result of an increased Li-SOCl<sub>2</sub> reaction rate within the cell. This could be caused by: (1) operating the cell at discharge rates which exceed the design range; (2) an external short of the cell; (3) a low impedance internal short circuit between anode and cathode; (4) lithium coming in direct contact with the carbon cathode.



The first three causes result in a temperature rise in the same manner, namely power from the cell, in the form of heat, is dissipated across loads internal to the cell. Thermal runaway can be prevented by the use of thermal fusing. Additionally, current limiting semiconductors, fusing, relays, and/or squibs can provide external short circuit protection. Internal shorts can only be avoided by designing to preclude them, followed-up by strict quality control.

As for the final cause of an increased cell reaction rate, lithium can come in contact with the carbon cathode in one of two ways. First, external heat applied to the cell will melt lithium at approximately  $356^{\circ}\text{F}$ . If the cell in question is even partially discharged, then the molten lithium could also combine with elemental sulfur, a by-product of cell discharge, and cause an explosion. It is for this reason that incineration is not recommended as a method of disposal. A molten lithium control does exist, however, to make the lithium cell safe, even when incinerated. It consists of a ceramic casing around the lithium anode which reacts with the molten lithium to produce a stable compound.

Voltage reversal is the second means by which lithium can come in contact with the carbon cathode. This normally occurs in a combination series/parallel connected battery package, where an inferior cell is driven by the other cells in the stack. It is then that lithium can be plated into the pores of a partially depleted cathode. By using a cathode



limited cell design, or diverting plating to a metallic substrate, this can be eliminated. Another solution would be the use of reverse current diodes to by-pass the internals of the problem cell altogether. Whatever course of action is taken, the occurrence of voltage reversal is dependent upon cell life history; therefore, individual cell monitoring is recommended [14,15,18].

There are options external to the cell/battery which can be implemented to increase safety as well. Separators between cells prevent the catastrophic failure of one cell from spreading to adjacent cells. In the event of battery venting to relieve pressure, the gases could be contained within a charcoal blanket surrounding the battery. Battery containment vessels are built to withstand an explosion and keep the battery's components intact. Additionally, if the battery internals were exposed to the atmosphere, potential hazards exist, lithium could burn upon exposure to moisture, and thionyl chloride could react with moisture in the air to produce acidic fumes. For this reason, the battery containment vessel also serves to protect the battery from any outside force which might otherwise crack or puncture the battery [17,18].

A safety program on lithium thionyl chloride batteries is documented in NAVSEANOTE 9310 entitled "Responsibilities and Procedures for the Naval Lithium Battery Safety Program". It covers the responsibilities, acquisition, design, use, packaging, handling, storage, and disposal of lithium



batteries. Transporting of lithium batteries is covered under DOT-E 7052, which is incorporated as part of NAVSEANOTE 9310 [31].

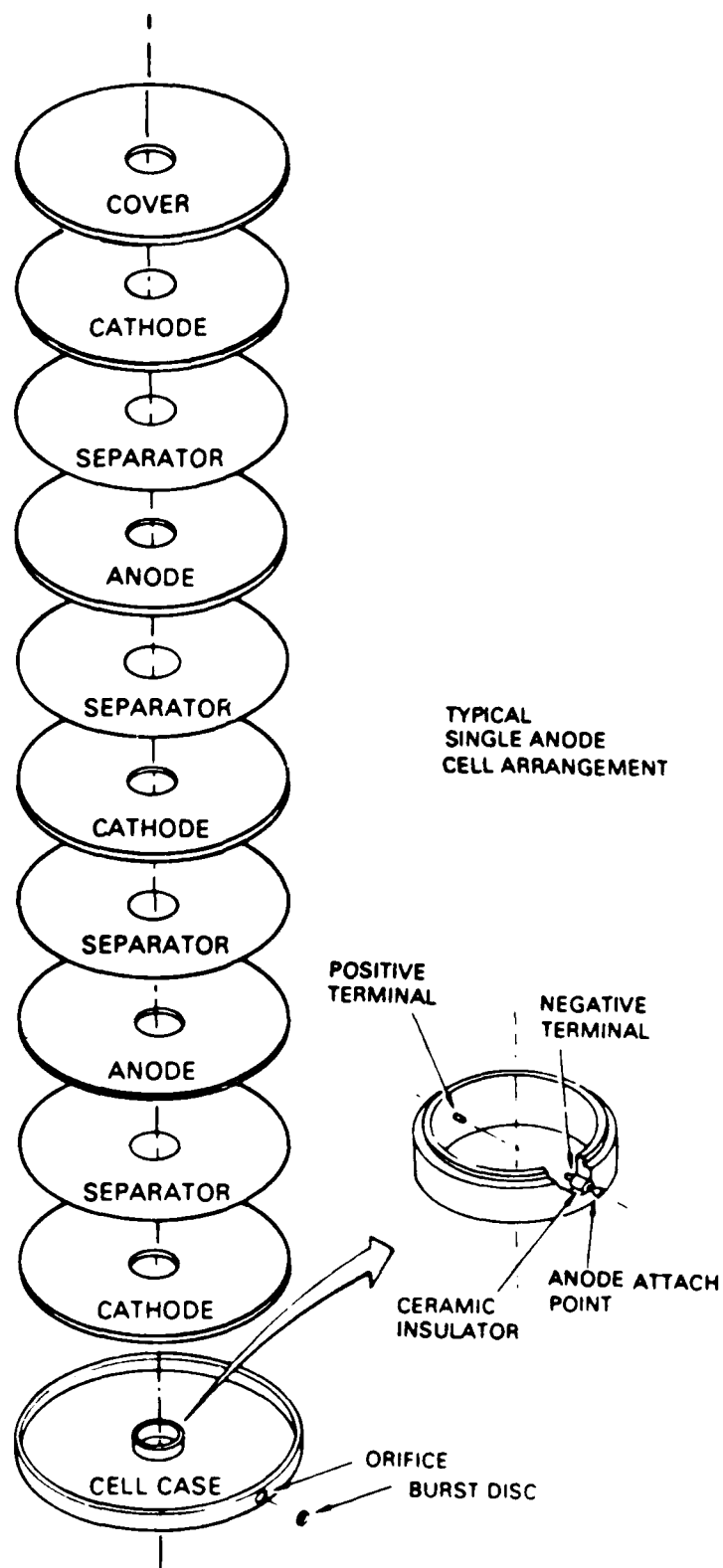
This program allows the use of lithium batteries only in situations where operational requirements dictate that no other battery will do. Additionally, the program addresses incorporating the specific application of the lithium battery into any decision about usage. For example, a battery of questionable safety used on a one-time basis for scientific purposes by highly skilled technicians might be viewed as acceptable, whereas a relatively safer battery to be used in extensive operations by unskilled personnel might be viewed as an unacceptable application of lithium batteries [13].

#### 3.4 INSTALLATION DETAILS

Off-the-shelf lithium thionyl chloride batteries do exist which would be suitable for the undersea vehicle described in Chapter 1. The most promising candidate is a high energy density battery (HEDB) developed at the ALTUS Corporation for NOSC San Diego. It consists of disk cells in a stacked arrangement (Figs. 3.1, 3.2). The resulting cylindrical battery was designed to fit into the existing fuel section of the Navy's MK 48 torpedo. Pertinent cell dimensions are contained in Table 3-1, while cell performance characteristics and testing results are contained in Table 3-2.

Since more than half the weight of each cell is the





ALTUS HEDB Disk Stack

Figure 3.1



TABLE 3-1

ALTUS HEDB CELL DIMENSIONS

Diameter (in)	17
Thickness	2
Weight (lb)	30
W-hr range	3300 - 6800
kW-hr/ft <sup>3</sup>	31.1
W-hr/lb	200
Amp-hr range	1000 - 2000
Internal impedance (milliohms)	6
Open circuit voltage	3.65
Useful voltage	above 2.5
Avg voltage @ 16A	3.44
Avg voltage @ 0.6A	3.55
Terminal configuration:	
- positive	Female threaded boss (center hole)
- negative	Male spade (outside circumference)

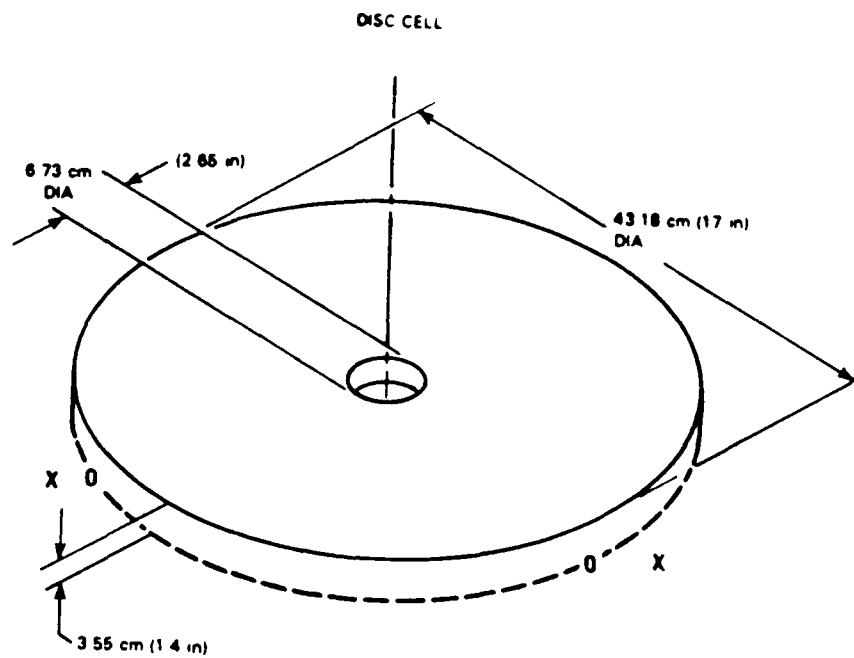


TABLE 3-2

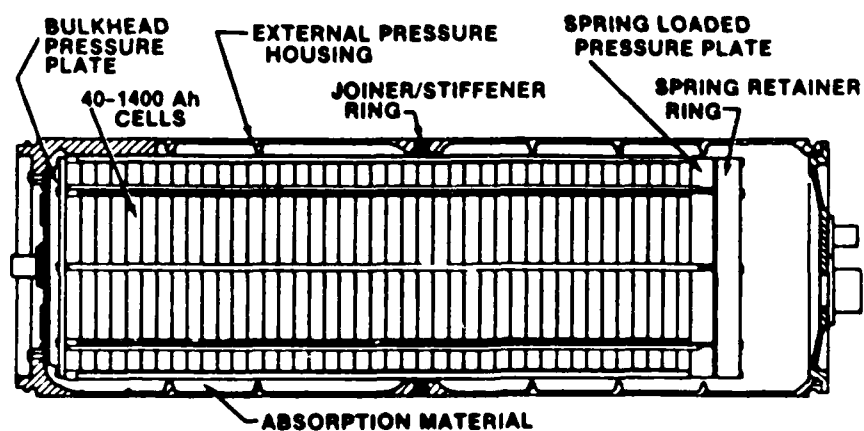
ALTUS HEDB PERFORMANCE CHARACTERISTICS

Stand-by to full power	< 5 min
Operating attitude	axis horizontal $\pm 35^\circ$
Temperature:	
Operate	28 to $81^\circ\text{F}$
Storage	-40 to $140^\circ\text{F}$ (activated) -40 to $167^\circ\text{F}$ (dry)
Environmental:	
Shock	MIL-B-18C Type II
Vibration	MIL-B-18C Type I & II
Pressure	1000 psi
Drop	3 ft
Safety:	
No mechanical failure under following conditions:	
Drop	6 ft
Short circuit	$\sim 0.01$ ohms (between + and - terminals)
Reverse voltage	$\leq 0.5$ V applied to a fully discharged cell @ $\geq 2\times$ rated A-hr
Penetration	Any part of cell, with exception of within 0.5 in of negative terminal
External heating	Avg temp rate of rise of case $100^\circ\text{F}$ per min from 160 to max $1000^\circ\text{F}$





ALTUS HEDB Disk Cell



ALTUS Battery Containment System

Figure 3.2



stainless steel case material, with the introduction of advanced casing materials on follow-up models, cell weight can be reduced from 30 lb to 20 lb.

The battery containment system has also been developed and consists of both an inner and outer structure (Fig 3.2). The inner structure provides for the assemblage and separation of the individual disk cell. The outer structure outside diameter is 21 inches which is again suitable for the Chapter 1 application. Figure 3.3 shows the ALTUS HEDB cell arranged to meet the requirements of this application. The fact that this structure is water tight would allow for a modular approach to vehicle construction, at least from an energy system standpoint. Additionally, there is adequate free volume to install activated charcoal to act as an absorbing agent for any cell exhaust products, should venting occur [17].

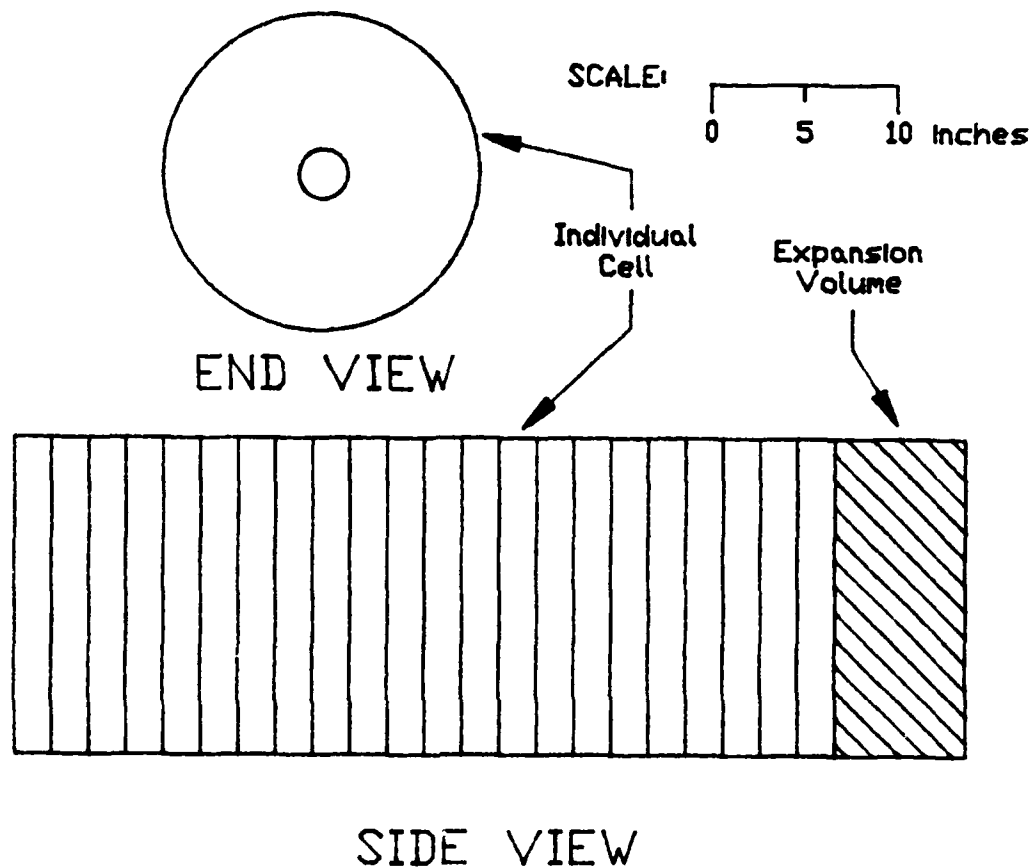
As for battery monitoring, ALTUS Corporation has developed a reliable, compact system using low cost, off-the-shelf technology. The system evolved around the ground-referenced differential amplifier. Figure 3.4 shows the monitoring system's block diagram [14].

### 3.5 CURRENT ASSESSMENT

Because of its disk shape, the ALTUS HEDB cell makes better use of available volume than the Yardney LR-190 silver-zinc cell. Because of this, and the fact that lithium thionyl chloride batteries have higher energy densities to



## ALTUS HEDB Cell INSTALLATION



Total No. of cells: 22

Total volume available: 11,576 cu in

Total volume used: 9,987 cu in

Total energy: 149.6 kW-hr

Total cell weight: 660 lbs

Figure 3.3



begin with, the ALTUS cell is better suited for the longer duration missions of Chapter 1. A realistic value of energy density, using the ALTUS HEDB cell (Fig. 3.3) is 12.9 W-hr/in<sup>3</sup> and 226.7 W-hr/lb.

There are some additional considerations when dealing with lithium thionyl chloride batteries. Up to this point, cost has not been mentioned, mainly because of the proprietary nature of such information. The prohibitive start-up costs of developing a battery to meet a specific application have confined the industry to a military customer base, for the most part. Since the application of Chapter 1 calls for an off-the-shelf design, start-up costs are not a factor. The additional costs of maintaining a strict quality control and a virtually humidity-free manufacturing environment, however, would add to the price of an existing battery. Industry spokesmen predict a 20-30% growth in the industry over the next decade as a reason for expected gradual cost reductions [12,14].

It is suggested that undersea applications be approved by the analysts who head the lithium battery program at the Naval Surface Weapons Center, White Oak. NSWC recommended that personnel involved in such projects consult with their analysts at the earliest possible convenience, in order to avoid the possibility of an applications problem being discovered after the developmental vehicle has already been designed and built [13].



NSWC's analysts offered a fairly optimistic view of the lithium battery industry. While they felt that the chemistry of the lithium thionyl chloride battery was not fully understood, they agreed with industry analysts in saying that they did not feel this should preclude the use of the battery, citing the lead-acid battery as an example. They expected improvements over the next five years which would make it possible to manufacture safer and more reliable lithium batteries. These improvements were expected to be significant enough to be noticeable by all those who deal with the real world applications of these batteries. The improvements themselves were expected to come in three major areas: chemical design and understanding, mechanical design and understanding, and manufacturing processes.

In the area of chemical design and understanding, it was felt that improvements were less likely to come over the course of the next five years and more likely to come in the next fifteen. These improvements, in areas such as changing the chemical balance or electrolyte of the cell, would lead to either actual improvements in the cell's performance and safety, or to an understanding of areas of cell performance to be avoided.

The area of mechanical design has already seen marked improvement, with better vent behavior for the cell already being achieved. Another improvement in this area has been in understanding and correcting a voltage delay problem which prevented the battery from delivering full power immediately



once a load was applied. This has been attributed to the build up of LiCl crystals on the lithium anode surface. Industry is currently working on eliminating this voltage delay by coating the anode with a thin, durable ethyl-2-cyanoacrylate polymer [13,14].

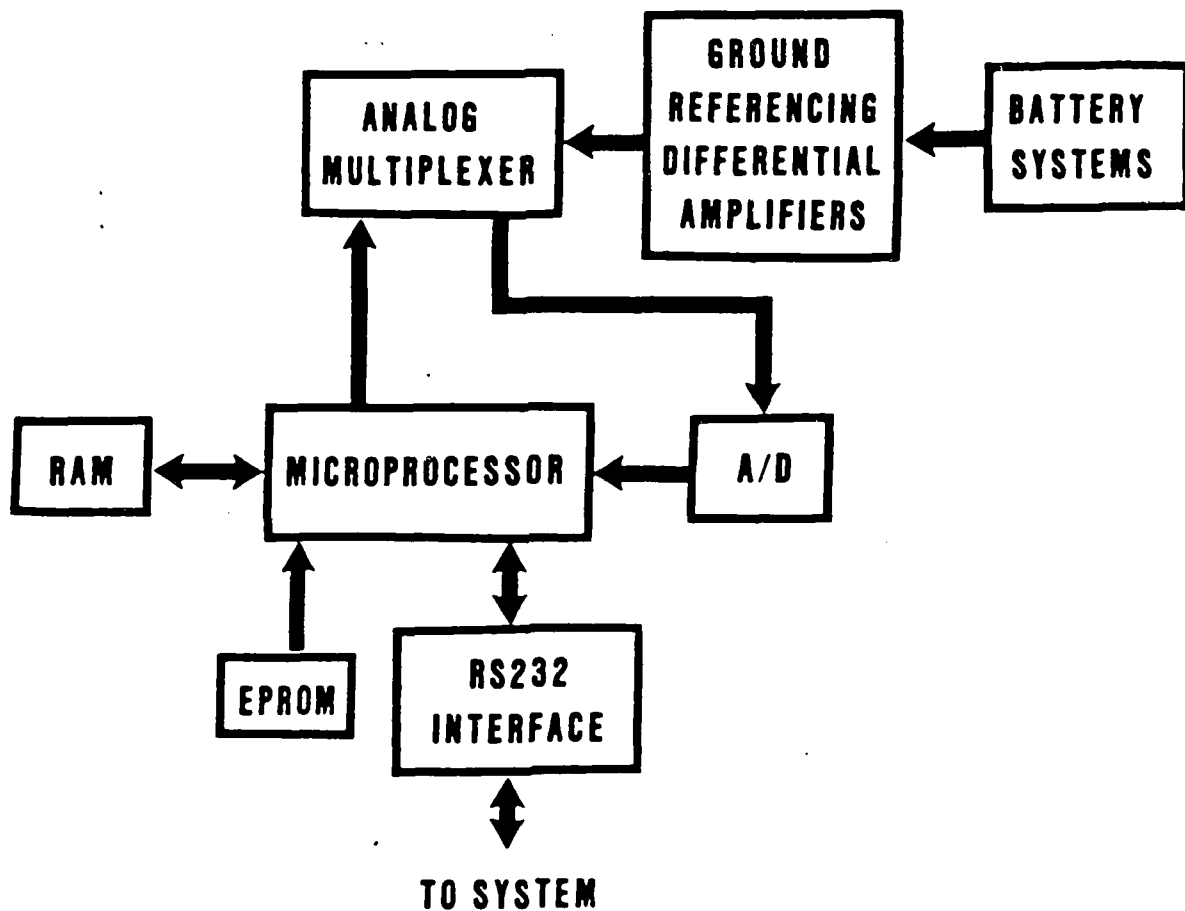
Finally, in the area of manufacturing processes, particularly quality control, improvements are expected as the industry executes a learning curve. Early on, many battery mishaps were attributed to internal short circuits which, in turn, were attributed to unmanufacturable design demands and quality control incompetence. An increased focus in this area alone has done much to improve lithium thionyl chloride batteries' recent record.

A final consideration discussed with NSWCC was the fire safety of the lithium thionyl chloride battery. Studies have shown that, not only are all shipboard firefighting agents ineffective in extinguishing a lithium fire, they often exacerbate the fire. These NSWCC analysts were quick to point out that the catastrophe which originally caused the lithium to be exposed to fire would present more of a concern to shipboard personnel than the resultant lithium fire [13,19].



## BATTERY MONITORING SYSTEM BLOCK DIAGRAM

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ALTUS Battery Monitoring System Block Diagram

Figure 3.4



## Chapter 4

### SODIUM-SULFUR BATTERIES

#### 4.1 INTRODUCTION

The sodium-sulfur battery is a relatively high energy density secondary battery (90 W-hr/lb) which operates at a high temperature (660°F). Development has been fairly recent, and has focused on specific application areas. Possible use of these batteries for utility load leveling has been sponsored in the US by the Electric Power Research Institute (EPRI). The Department of Energy (DOE) has sponsored research in the area of electric vehicle applications. Specific vehicle applications have been railway cars as well as smaller commuter cars [20].

Drawbacks of the sodium-sulfur technology are associated with its requirement to maintain high enough temperatures to keep the liquid metal electrodes molten, while at the same time not over heating. The requirements for insulation and cooling, as well as compartmentalization to prevent the spread of a chain reaction from an individual cell failure, add significantly to the weight and volume for this energy system. Consequently, it is somewhat less competitive from an energy density standpoint.

#### 4.2 TECHNICAL DESCRIPTION

The sodium-sulfur cells use electrodes of molten sodium and sulfur with a solid electrolyte. Only two materials have been found with good ionic conductivity, zero electronic

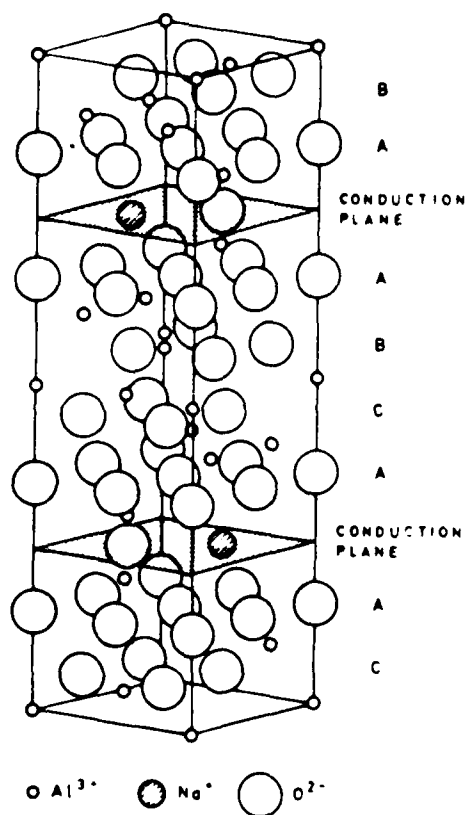


conduction, impermeability, resistance to chemical corrosion with the cell reactants, and sufficient mechanical strength: borate glass and beta alumina.

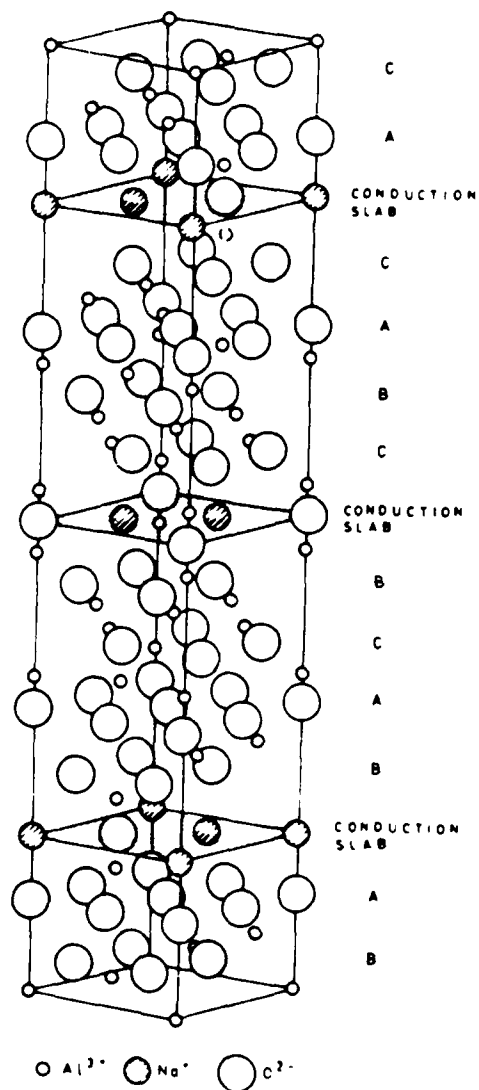
Little information has been published on the borate glass or Dow cells. Because the resistivity of the glass is about three orders of magnitude higher than beta alumina, thin walled capillary tubes of glass are used. The glass is drawn into hollow fibres of diameter 3.6 microns and wall thickness 0.4 - 0.6 microns. Chloride is added to improve conductivity. In order to prevent the deleterious effects on glass of oxides and hydroxides of sodium, getters such as zirconium titanium alloys are used. Calcium is harmful as well, so the amount present in the sodium must be kept to a minimum. Because minute platinum particles cause cracking in glass fibres, the level of oxygen in the glass melt must be kept sufficiently high to prevent dissolved platinum oxide from precipitating as platinum.

The most widely used solid electrolyte is the crystalline solid, beta alumina which comes in two distinct forms. Though their chemical composition  $(\text{Na}_2\text{O})_{1+x} 11\text{Al}_2\text{O}_3$  is the same, their crystalline structure is different. Beta alumina has a two-fold screw axis (two block) structure while beta" alumina has a three-fold screw axis (three block) structure (Fig. 4.1). Beta" alumina has a lower resistivity than beta alumina at temperatures of operation, but because it is unstable at temperatures  $> 2820^\circ\text{F}$ , stabilizing dopant materials such as magnesia and lithia are used during





Beta alumina  
Crystalline Structure



Beta'' alumina  
Crystalline Structure

Figure 4.1



fabrication. Levels of dopant are below 2% as the level of dopant does affect electrolyte stability. The manufacturing process for this solid electrolyte involves a three step procedure:

- 1) Powder process involving dry milling of components
- 2) Shaping the powder, either by isostatic pressing or electrophoretic deposition
- 3) Sintering in a controlled environment, using either a pass-through or batch firing technique

The sodium electrode has two requirements for satisfactory operation: (1) solid electrolyte must be in complete contact with the molten sodium, and; (2) minimum beta" alumina/sodium interface polarization. The first requirement is normally achieved by one of three methods: (1) sodium gravity feeding from a reservoir; (2) sodium wicking; (3) forcing from a sodium reservoir by gas pressure. The second requirement is a complex one, directly related to the purity of both the sodium and the beta" alumina.

In the sulfur electrode, a choice of materials for the current collector is important due to the corrosiveness of the polysulfide melts. In both the borate glass and beta" alumina electrolyte cells, aluminum rods are used. To protect against an insulating film of aluminum sulfide, carbon or molybdenum coatings are applied to the rod. In the central sodium cells, where the outer cell casing acts as the current collector, steel is normally used instead of aluminum to protect against a compromise of cell integrity during a failure [21].

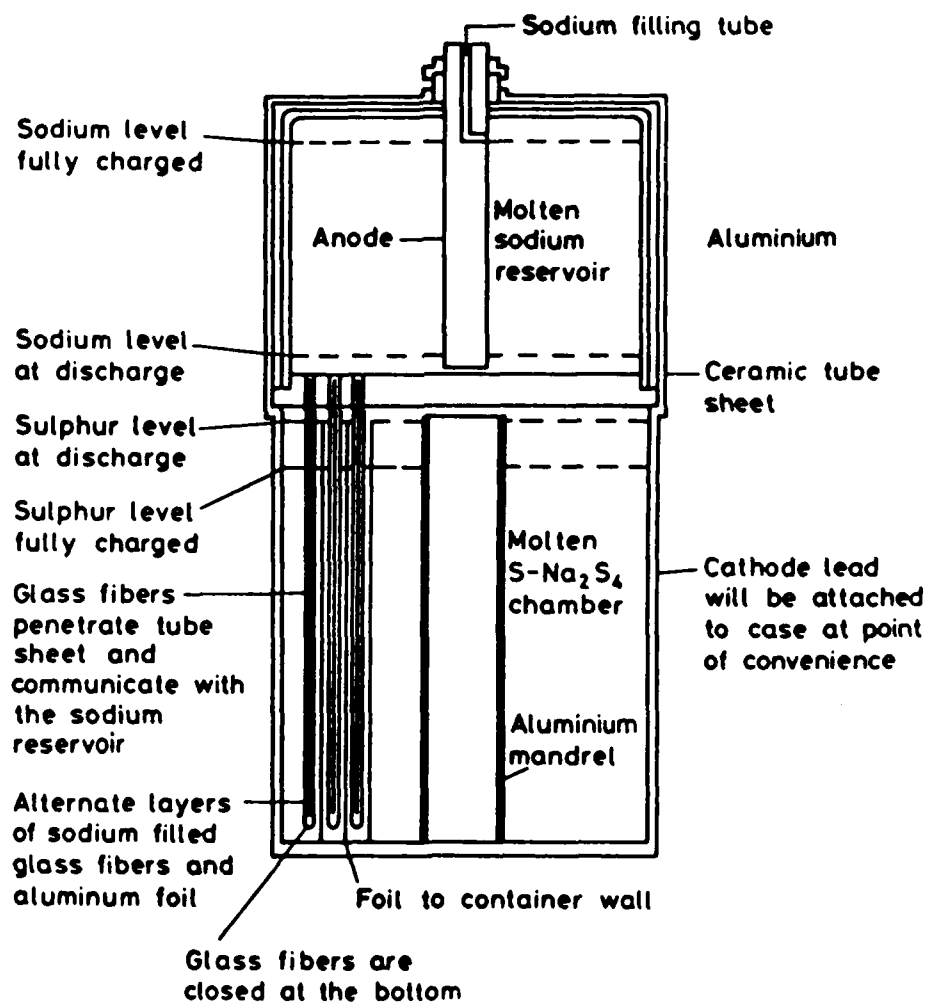


There are four main cell types: (1) Dow cell; (2) plate cell; (3) central sodium cell; (4) central sulfur cell. The Dow cell (Fig. 4.2) is the only cell type to make use of the borate glass electrolyte. It was developed by Dow Chemical, because of their expertise in glass fibre technology, as an in-house load leveling device. Cell failure and safety problems are a disadvantage with this cell type, but these must be weighed against the lower raw material and production costs of borate glass over beta" alumina.

The plate cell (Fig. 4.3) is superior to tube cell designs in the following areas: cell packaging, thermal control, safety, ease of assembly, cell orientation, mass production of electrolyte, and quality control. Unfortunately, its areas of shortcoming, sealing and mechanical strength, are major and have yet to be resolved. As a result, the plate cell design has been confined to laboratory testing applications.

The central sodium cell (Figs. 4.4 & 4.5) has the highest energy density of the tubular designs. Its disadvantage is related to the fact that, in this design, the cell casing acts as the current collector. Because the current collector requires protection from polysulfide corrosion, the cell case would either have to be made of a corrosion resistant material, or it would have to be coated as discussed in an earlier paragraph. Either method would be difficult.

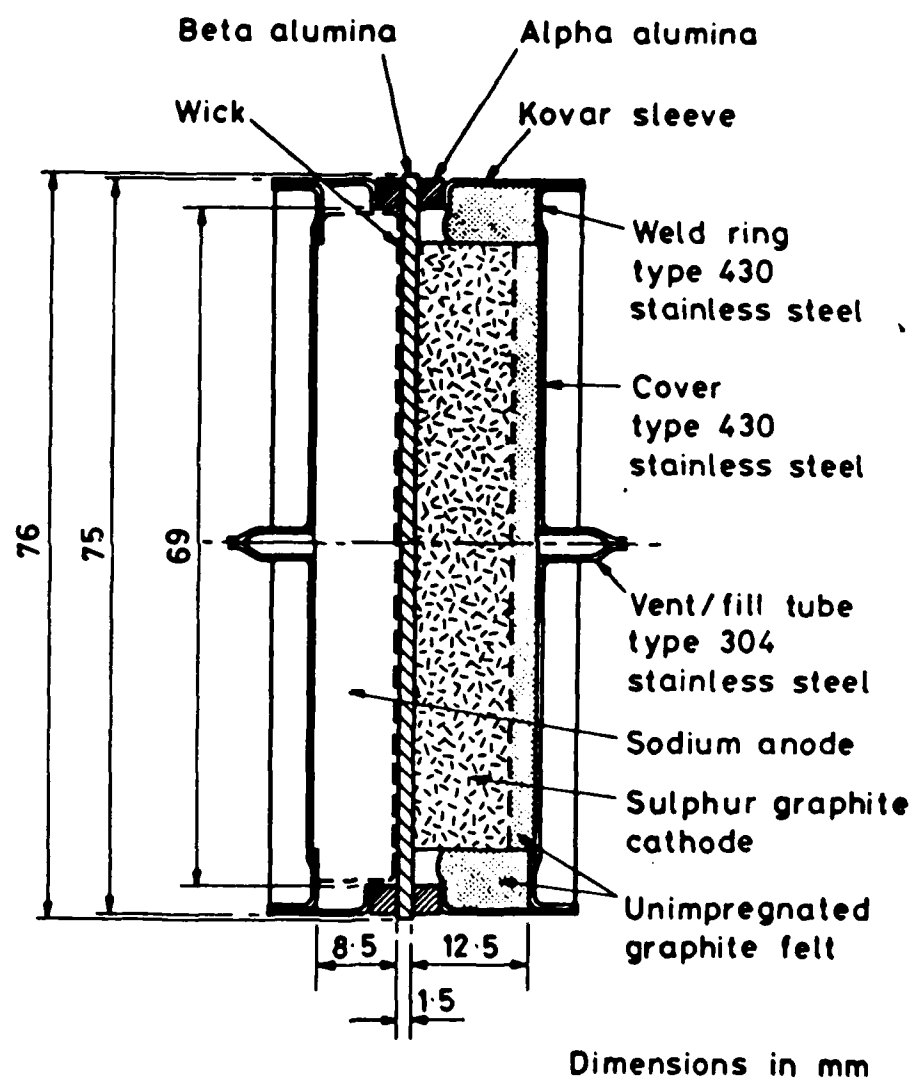




The Dow Cell

Figure 4.2

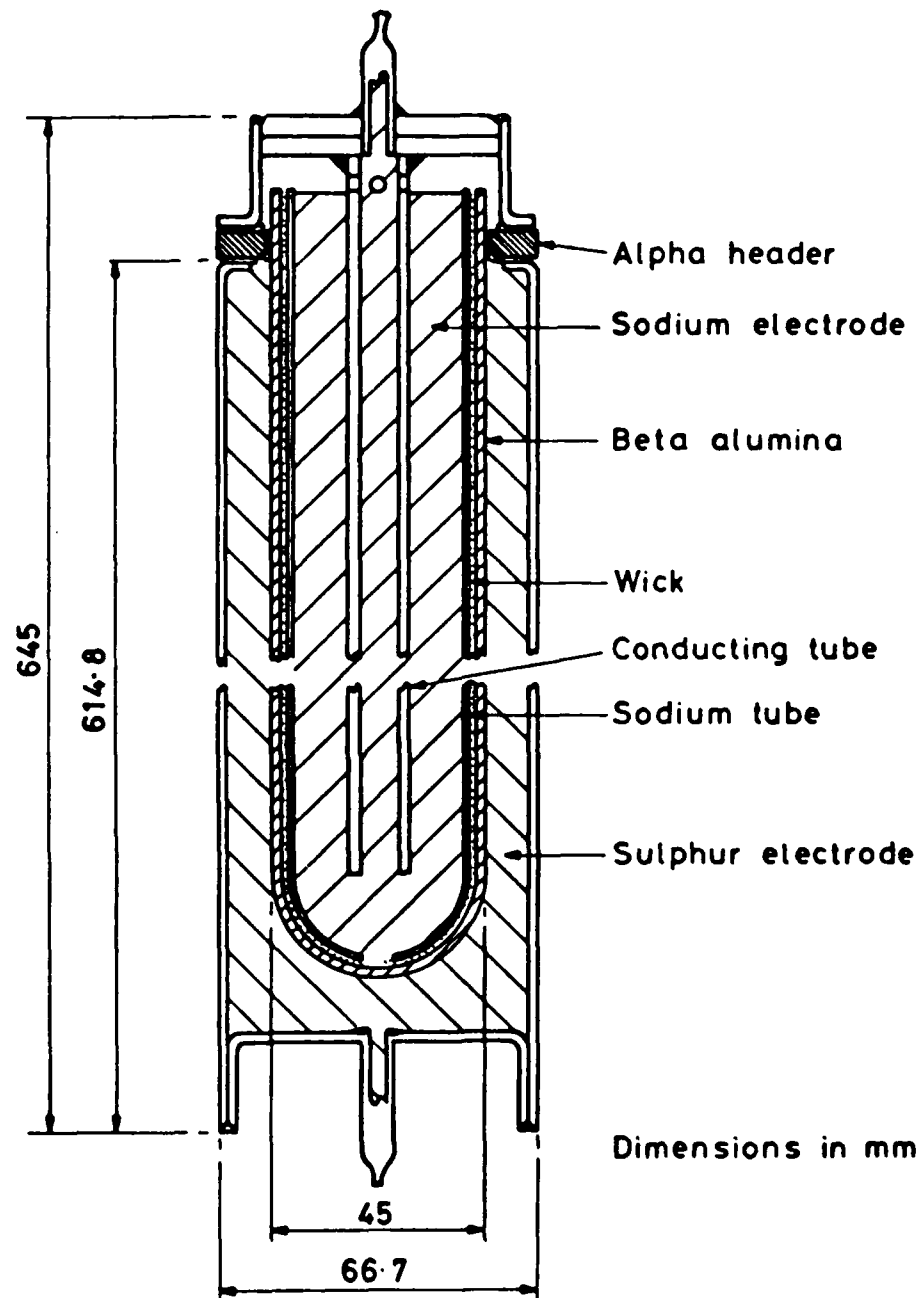




The Plate Cell

Figure 4.3

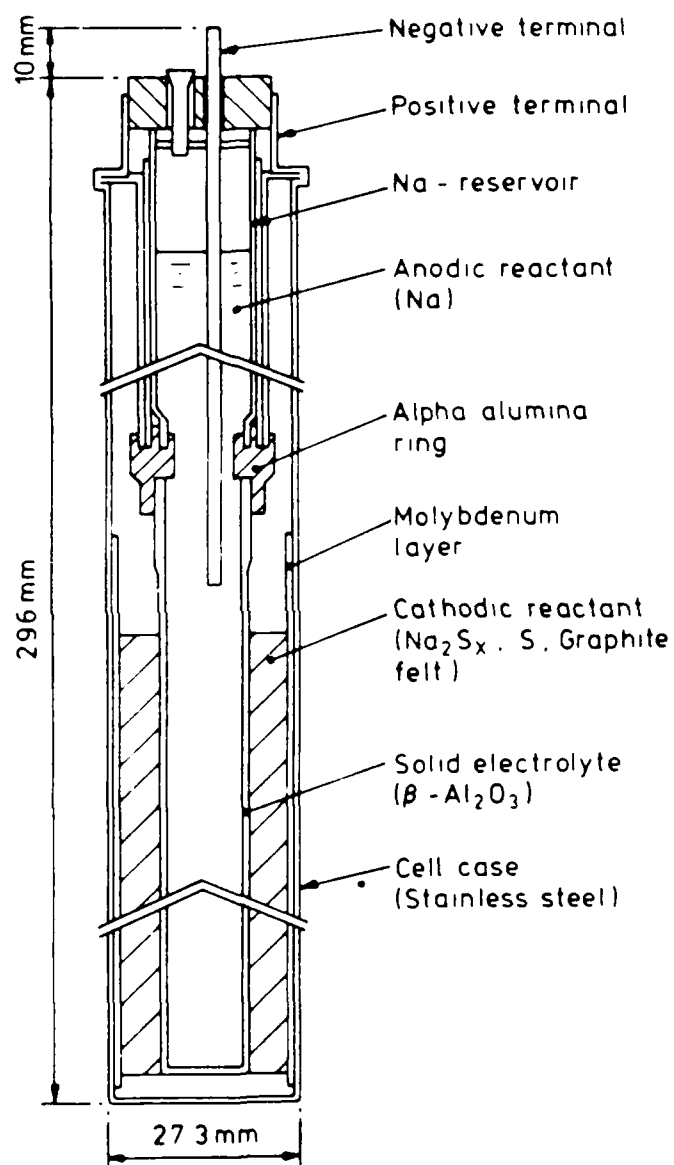




The Central Sodium Cell with Sodium Wick

Figure 4.4





The Central Sodium Cell with Sodium Reservoir

Figure 4.5



The central sulfur cell design (Fig. 4.6) uses an easily coated rod as a current collector. Other advantages over the central sodium cell type include:

- Mild steel can be used for outer casing instead of more expensive steel or superalloy because the outer cell contains only liquid sodium
- Better separation of sulfur and sodium reactants resulting in a safer cell design in the event of beta" alumina failure
- Greater electrolyte area per volume than central sodium cell resulting in higher peak power output

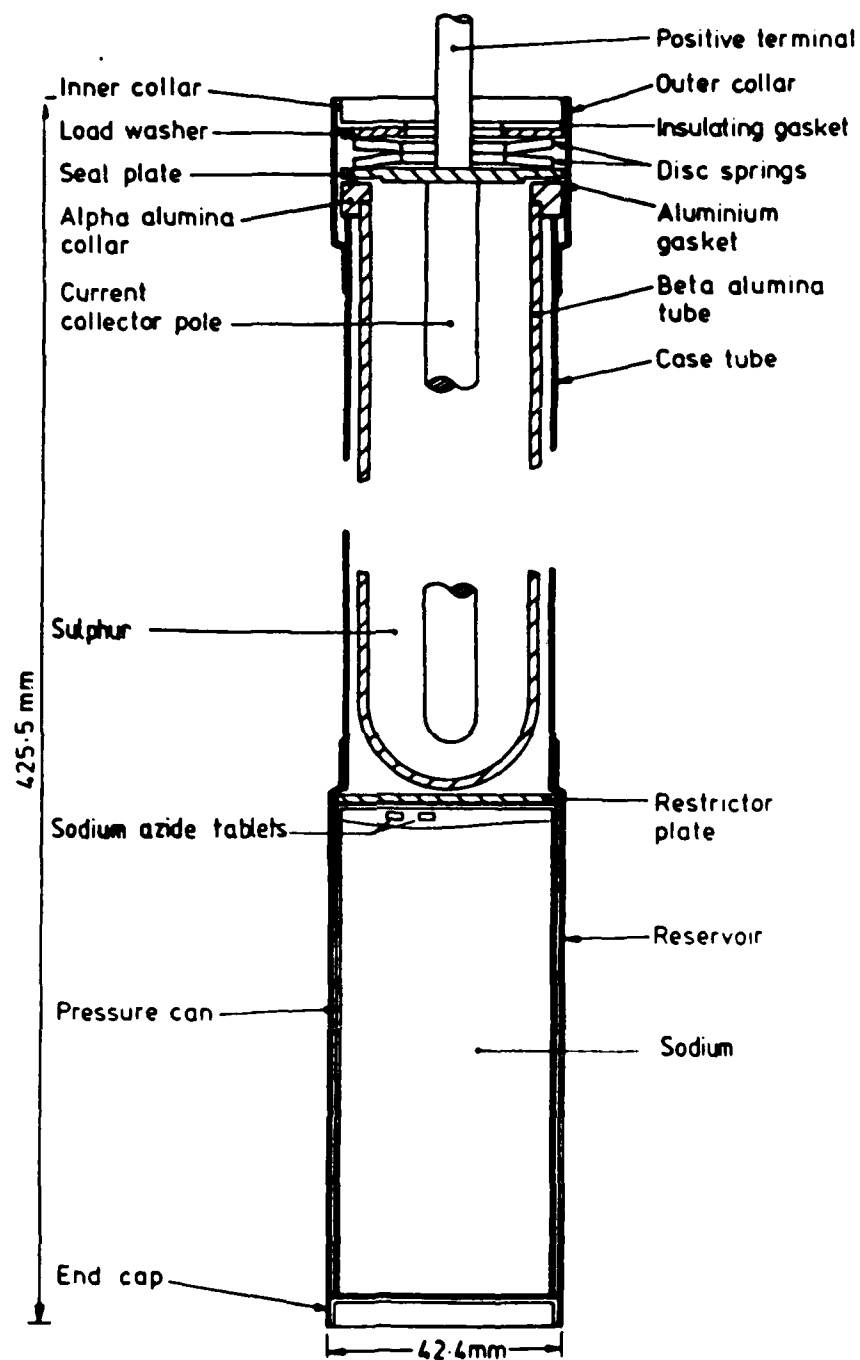
The seals are more complex in the central sulfur cell, however. A comparison of the various cell types is summarized in Table 4-1 [21].

#### 4.3 SAFETY

The safety of sodium-sulfur cells is dominated by concerns about the volatile nature of the cell reactants. Safety concerns are addressed in actual cell design by precluding, or at least limiting the occurrence of known hazardous situations. Anticipating safety-related misgivings about such a high energy battery, particularly in vehicle applications, the industry focused on safety research in the mid-1970's.

The chain of events which lead to cell failure most often begin with failure of the solid electrolyte, for which the causes have already been discussed. These causes are best controlled by using quality materials and strictly controlled procedures in the manufacturing process.





The Central Sulfur Cell

Figure 4.6



TABLE 4-1

## CELL TYPE COMPARISON

	<i>Glass electrolyte</i>	<i>Beta alumina electrolyte cells</i>			
	<i>Dow</i>	<i>Plate</i>	<i>Central sodium tubular</i>	<i>Central sulfur tubular</i>	<i>Multitubular</i>
Performance	Acceptable	Low but acceptable for very high rate applications	Very good	Acceptable	Good
Construction and sealing	Difficult	Difficult	Easy	Relatively easy	Difficult but acceptable for small assemblies
Corrosion	Still some problems	No solution demonstrated for flexing bipole construction	Cost effective solution not yet demonstrated	Corrosion resistant pole developed	As comments on central sodium and central sulfur
Safety	Questionable	Good	Questionable with large cells	Good	Not yet demonstrated
Cost prediction	Low	Acceptable	Depends on case corrosion solution	Acceptable	Unacceptable for large multitubular assemblies



In the event of solid electrolyte failure, the next major concern is the molten sodium and sulfur coming into contact with one another on a large scale. The focus, therefore, becomes cell designs which separate the bulk of the reactants and limit the quantities which can immediately react upon electrolyte failure.

The final step in the cell failure is the large scale reaction of sodium and sulfur resulting in extreme temperatures and cell rupture, either through high pressure bursting, or high temperature sodium polysulfide corrosion of the cell casing material. As the temperature increases to approximately 1290°F, a point is reached where the sulfur vapor pressure exceeds the bursting pressure of the cell casing. A solution to this problem is to eliminate the free sulfur, either by discharging the cells, or by combining the sulfur with other chemicals. High temperature sodium polysulfide corrosion of the cell casing is prevented by coating the casing material. If the casing is to act as the current collector, as in the central sodium cell, the coating material has the added requirement that it must be conductive. Graphite paper has proven to be the most effective in all areas. Its only disadvantage is its high cost [21].

A safety concern in battery applications is the propagation of a single cell failure to adjacent cells, or to the environment. Cell separation materials and battery containment vessels address this concern.



#### 4.4 INSTALLATION DETAILS

The requirement for the sodium-sulfur electrodes to be molten poses a problem for undersea applications of this battery. The normal operating temperature of the cell is enough to keep the electrodes molten, and short periods of inactivity can be withstood using insulation, or electric resistance heaters. Although the frozen electrode of a long dormant cell can be thawed using a thermal match, the long term effects of the freeze/thaw cycle on cell performance are not understood at this time [21].

An additional thermal management problem facing the user of sodium-sulfur cells is the requirement to cool a cell during normal operation to prevent overheating. In an undersea application, forced air cooling with heat transfer to the sea water through the vehicle's skin is certainly possible. However, the adverse impact on the battery's overall volume makes it somewhat less attractive from the energy density standpoint.

#### 4.5 CURRENT ASSESSMENT

No off-the-shelf battery exists at this time which is suitable for the undersea vehicle application described in Chapter 1. The industry expects commercialization within the next two years, with production costs that are competitive with the lead-acid battery. With respect to battery safety and testing, it is worth noting that, though vehicle testing was a success with no major safety problems, the testing was



conducted on a limited scale, under controlled conditions, by highly skilled professionals. An extensive, operational application with less skilled personnel might yield less satisfactory results.



## Chapter 5

### FUEL CELLS

#### 5.1 INTRODUCTION

The recent development of fuel cells began with the Bacon cell described in the 1950's. The fuel cell has seen use in various military and space applications, in submersibles, and has been considered for automobiles and trains. More recently, development has focused on extending the life of high (MW) output fuel cells so that the large capital investment for utility applications could be spread over many years [22].

Fuel cells use the chemical energy released in the reaction between a fuel and oxygen. Though its operation is similar to a conventional battery, the fuel cell's anode, cathode and electrolyte are not consumed, which, when combined with an uninterrupted supply of reactants, give it a theoretically unlimited life. Its high energy conversion efficiency (60-80%), combined with all the advantages that it shares with batteries, would seem to make the fuel cell a clear favorite among candidates for undersea vehicle applications. Unfortunately, in the case of this specific undersea vehicle application, the requirement to store enough reactants for an extended run, as well as to store the products generated, make the fuel cell considerably less attractive from a volume impact standpoint [23].

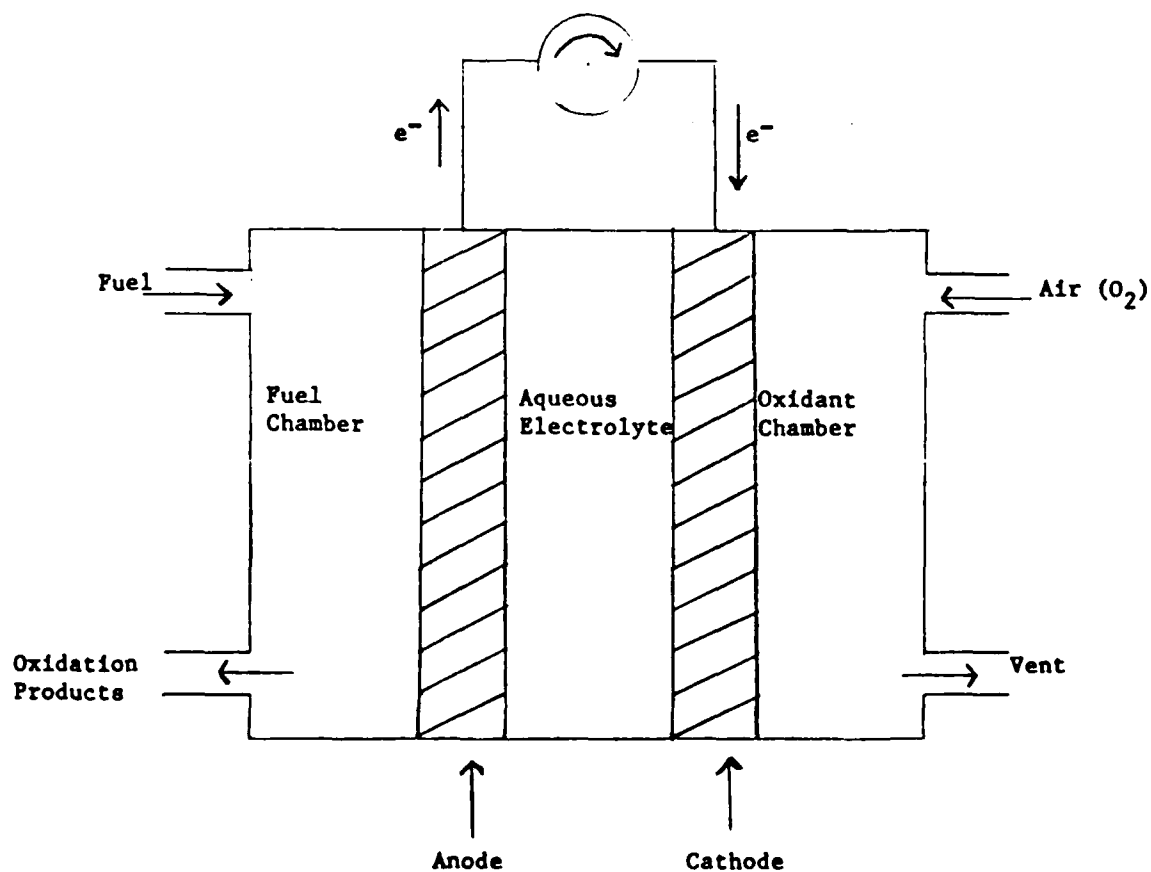


## 5.2 TECHNICAL DESCRIPTION

Hydrogen-oxygen fuel cells have the highest theoretical output, with an expected potential of 0.8 - 1.2 volts for the cell. The operation of such a fuel cell, like a battery, requires an electrolyte which does not conduct electrons, but allows ions to migrate. For an alkaline cell, the electrolyte is normally KOH. Cell reactions, and a representative cell schematic are shown in Figure 5.1. Alkaline cells can be sensitive to trace amounts of carbon dioxide, which leads to carbonate formation and a gradual loss of output. The hydrogen and oxygen can be stored in either cryogenic liquid form (Space Shuttle), or as high pressure gas (DSRV). Oxygen can also be stored in compound form as peroxides, superoxides, or ozonides. The mass of water that results from the cell reaction is equal to the amounts of reactants consumed, an important ballasting consideration for undersea vehicle applications [3].

Solid polymer electrolyte fuel cells use a sulfonated fluorocarbon similar to Teflon as the electrolyte. Such cells can withstand high pressure, and because there is no free electrolyte, leaking is not a concern. While solid polymer electrolyte cells are not sensitive to carbon dioxide, they do require platinum, which can add \$550/Kw to the cost of a cell [23].





Representative Fuel Cell

#### FUEL CELL REACTIONS

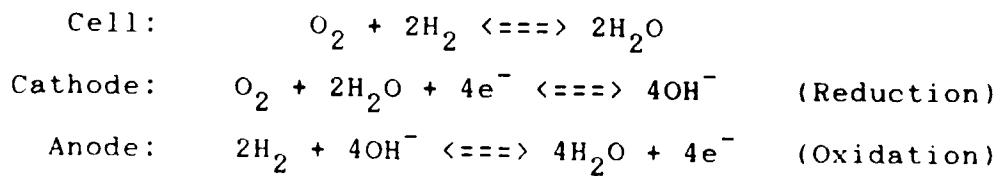


Figure 5.1



In the hydrazine-hydrogen peroxide fuel cell, hydrazine fuel is injected into the electrolyte and circulated across the anodes while hydrogen peroxide oxidant is injected into the electrolyte and circulated across the cathodes. The injection rate of both hydrazine and hydrogen peroxide is proportional to the applied cell load. Products of the cell reaction, in the form of hydrogen, nitrogen, oxygen, and ammonia, are produced at the rate of  $33.2 \text{ ft}^3/\text{kW}$  which is a distinct disadvantage in undersea applications. Additionally, early cells were limited to approximately 500 hours usage due to the blistering of the fuel cell's semi-permeable membrane that chemical oxidation caused. The applications of these three fuel cell types are summarized in Table 5-1 [23].

The high ideal fuel cell efficiency is often confused with overall system efficiency. The reality is that, internal cell resistance losses, as well as pumping losses associated with reactants and products, reduce the overall efficiency.

### 5.3 SAFETY

Primary safety concerns associated with hydrogen-oxygen fuel cells deal with the handling and storage of the reactants. Concentrations of hydrogen as low as 8% in the presence of air could result in explosion. Seals, gaskets, piping, storage containers, and transfer pumps must be able to withstand either high pressures or cryogenic temperatures



TABLE 5-1

FUEL CELL TYPES AND THEIR APPLICATIONS

ALKALINE

1.4 Kw	APOLLO
7 Kw	Space Shuttle
20 Kw	DSRV

SOLID POLYMER

1 Kw	GEMINI
3 Kw	Navy's High Altitude Super-Pressure Aerostat
5 Kw	NASA

HYDRAZINE-HYDROGEN PEROXIDE\*

5 Kw	Manned submersible
10 Kw	Block module

\* France



reliably. Unlike other energy systems already discussed, the consequence of fuel cell failure is the loss of output, not a catastrophe.

#### 5.4 INSTALLATION DETAILS

The fuel cell industry has consistently lagged behind the battery industry in the area of applications. The primary reason for this is cost. As a result, off-the-shelf fuel cell models do not exist; fuel cells tend to be custom designed for each specific application. Nevertheless, a survey of the major fuel cell manufacturers yielded a fuel cell with suitable dimensions and performance characteristics. The fuel cell, named "ORBITER" for its space applications, is manufactured by United Technologies Corporation and has the characteristics listed in Table 5-2. A spokesman for United Technologies indicated that the ORBITER's output of 12 kW could be decreased with minor modification to meet the undersea vehicle application described in Chapter 1. Volumes for the reactants and products, which is an important consideration to that application, are projected for various storage configurations in Table 5-3 [23,25].

#### 5.5 CURRENT ASSESSMENT

The use of noble metals as catalysts in fuel cells makes the cost prohibitive in all but the most specialized applications. For this reason, fuel cells have seen use



TABLE 5-2

"ORBITER" FUEL CELL CHARACTERISTICS  
UNITED TECHNOLOGIES CORPORATION

Power range (kW)	2 - 12
Output voltage	27.5 - 32.5
Weight (lbs)	255
Expected life (hrs):	
- unrefurbished	2500
- refurbished every 500 hrs	5000
Size (in):	
- length	48
- diameter	18
Efficiency	63%
Reactants	cryogenic O <sub>2</sub> & H <sub>2</sub>



TABLE 5-3

## REACTANT WEIGHTS AND VOLUMES

CELL AND STORAGE TYPE	ELECTROLYTE	lb/kW-hr	in <sup>3</sup> /kW-hr
Hydrogen-Oxygen:			
Cryogenic	KOH	1.01	70.2
High Pressure	KOH	5.43	118.4
Cryogenic	Solid Polymer	1.25	91.5
Hydrazine- Hydrogen Peroxide	KOH	8.8	231.9



mainly in military and space applications where energy system weight and/or volume were more of a concern than capital outlay. Unless there is a drastic rise in fossil fuel costs, making fuel cells much more attractive than internal combustion engines from a cost standpoint, the noise and atmospheric pollution-free operation of the fuel cell will not be enough to cause its widespread use in road and railway vehicles. Not much hope is seen in the near future for research in the area of fuel cell improvement; expensive research is only being performed by the utility industry for large scale load leveling applications.



## Chapter 6

### OTHER ENERGY SYSTEMS

#### 6.1 INTRODUCTION

There are other energy systems which have been determined to be feasible for an undersea vehicle application by earlier studies [1,2,3]. None of these systems were chosen for the undersea autonomous vehicle application specified in Chapter 1 because they all had the same shortcoming . . . they were too developmental at this time. Despite the fact that these energy dense systems had experience in other applications, further development and testing would be required before they could be applied to undersea vehicle applications.

#### 6.2 LITHIUM SULFURHEXAFLUORIDE THERMAL POWER PLANTS

The lithium sulfurhexafluoride combustor could be combined with a small, closed cycle Brayton engine to provide power for an undersea autonomous vehicle. A suitable engine is the Mini Brayton Rotating Unit (BRU) manufactured by Garret AiResearch for NASA. This particular application has already been covered in detail by both Labak and Sydnor [4,5], so it will not be discussed here.

In addition to the Brayton engine, the lithium sulfurhexafluoride combustor could be combined with either a small Stirling engine or an organic Rankine cycle. Stirling Thermal Motors, Inc., manufactures the STM1-120 Stirling



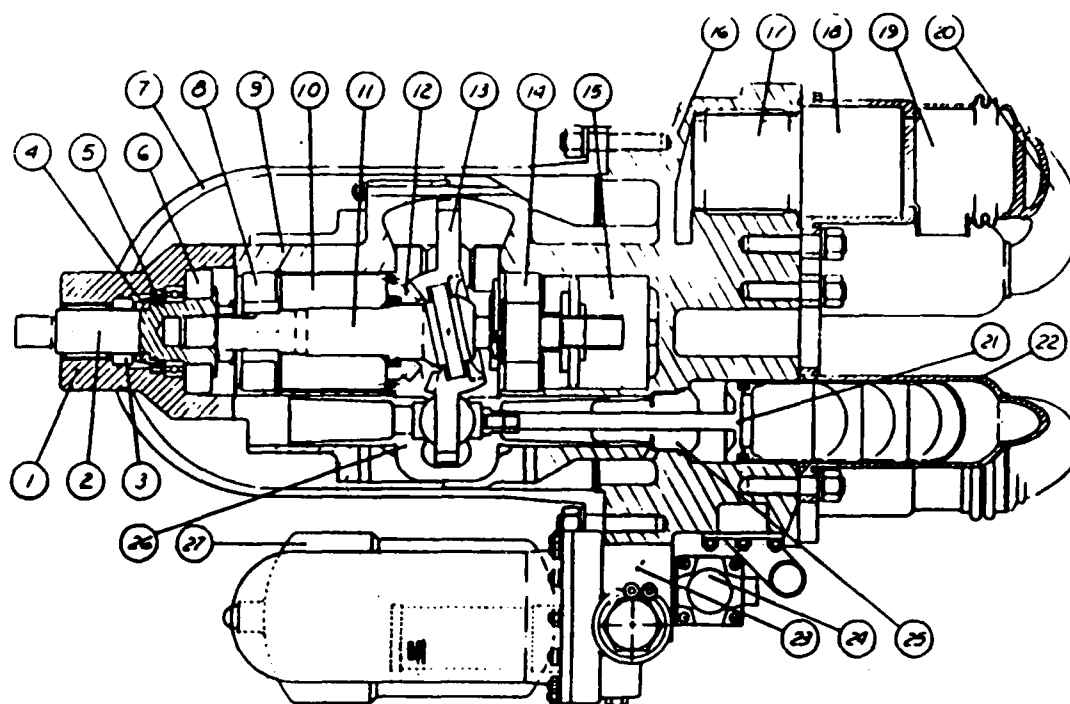
motor for this purpose [26,27,28]. The STM4-120 gets its designation from the fact that it is a variable swash plate drive, four cylinder engine with 120cc of swept piston volume (Fig. 6.1). The engine itself is roughly cylindrical in shape, with a diameter and length of 14 and 36 inches respectively. The output is 20 kW, but it can be throttled back to 5 kW. It is currently in the bench testing phase of its development. The Stirling engine would probably be more suitable for the 30/25 inch vehicle described in Chapter 1, but is not expected to be superior to the Brayton cycle unit.

The third option for the lithium sulfurhexafluoride combustor is an organic Rankine cycle (ORC). This type of cycle is used in the Dynamic Isotope Power System (DIPS) for space applications [29]. This ORC (Fig. 6.2) was designed to operate from 0.5-2 kW, but could be extended to 5 kW without major modification. The working fluid is Dowtherm A, and it operates at a temperature of 700°F. Though this system is also more appropriate for the larger vehicle size, it is expected to be less efficient than the Brayton cycle unit.

### 6.3 RADIOACTIVE ISOTOPE SYSTEMS

Of all energy systems considered, the ones with the highest energy density by far were the radioactive isotope systems. These systems too have seen application in space and have been discussed for undersea vehicle applications as well [29,30]. In addition to the DIPS discussed in the previous paragraph, Boretz has discussed an organic Rankine cycle electric power system (ORCEPS) based on Pu-238 [30].



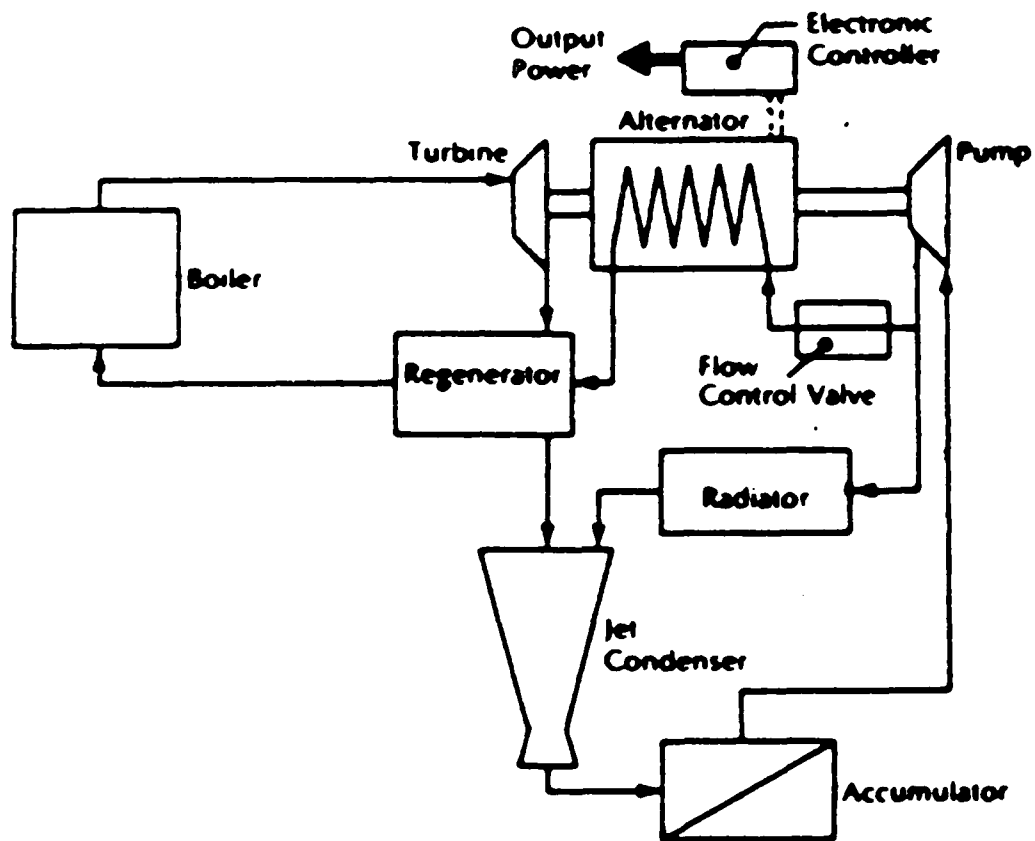


- |                                 |                        |                                   |
|---------------------------------|------------------------|-----------------------------------|
| 1) Rotating shaft seal assembly | 10) Rotary actuator    | 19) Heater                        |
| 2) Drive shaft                  | 11) Main shaft         | 20) Hot connecting duct           |
| 3) Rotating shaft seal          | 12) Bevel gear         | 21) Piston assembly               |
| 4) Mating ring                  | 13) Swashplate         | 22) Cylinder/regenerator housing  |
| 5) Radial lip seal              | 14) Front main bearing | 23) Hydraulic service assembly    |
| 6) Thrust bearing               | 15) Oil pump module    | 24) Power control valve           |
| 7) Pressure hull                | 16) Front crankcase    | 25) Oil scraper/cap seal assembly |
| 8) Rear main bearing            | 17) Cooler             | 26) Crosshead                     |
| 9) Rear crankcase               | 18) Regenerator        | 27) Accumulator                   |

STM1-120 Stirling Engine

Figure 6.1





Organic Rankine Cycle (ORC) for DIPS

Figure 6.2



The Rankine cycle uses Toluene for an output of 2.5 kW. A representative cycle is shown in Figure 6.3. The drawback with these systems is the fact that the isotopes are constantly producing heat. In an undersea application, the sea provides a ready cooling medium, but during handling and storage, or if a vehicle beached itself or was hauled up in a fishing net, the consequences of such a constant heat source without adequate dissipation would be unacceptable. The negative political and environmental climates surrounding such a system would also outweigh any potential energy

density gains.

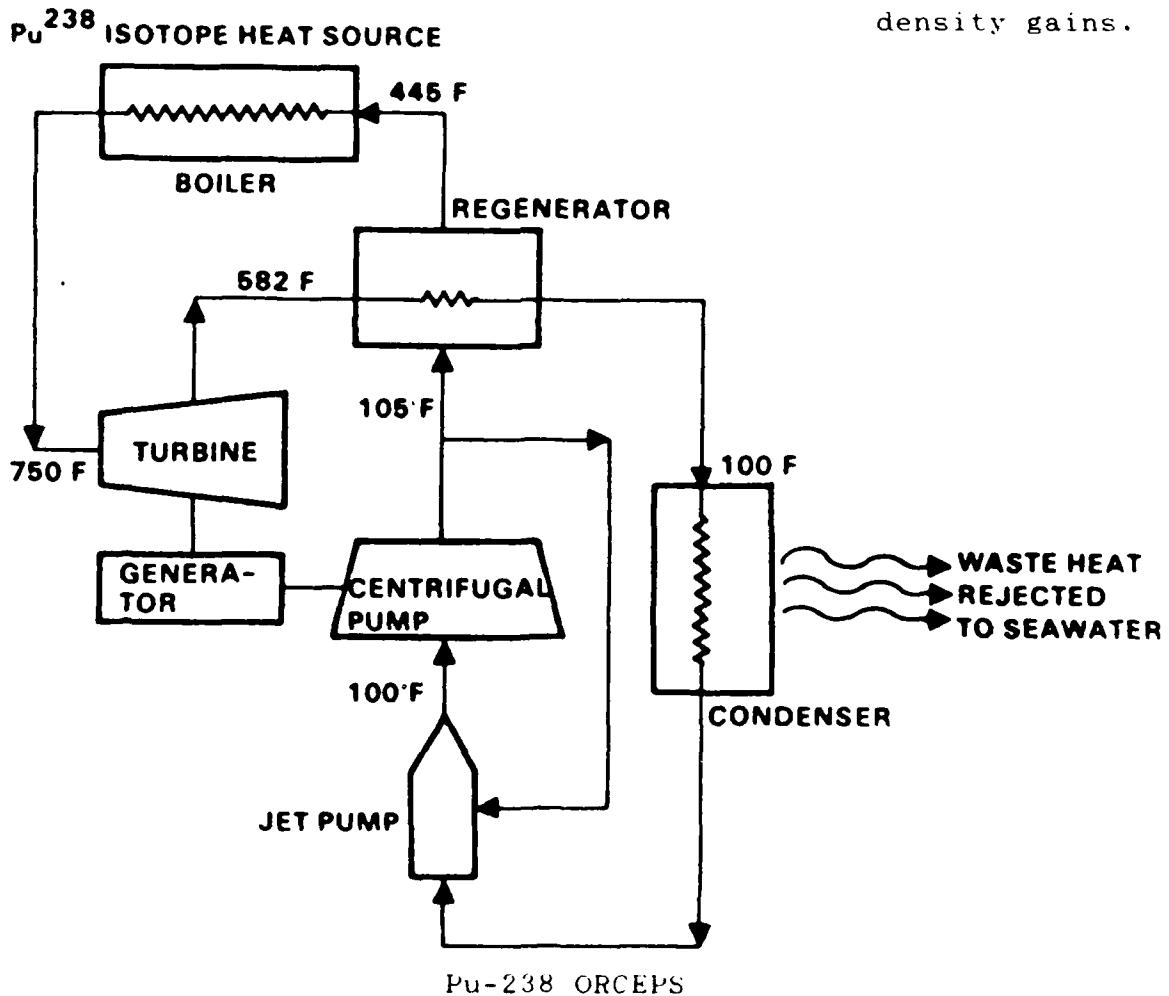


Figure 6.3



## Chapter 7

### CONCLUSIONS AND RECOMMENDATIONS

#### 7.1 INTRODUCTION

Given the specific requirements of Chapter 1 for a small, undersea autonomous vehicle, an energy system can be chosen from feasible candidates and designated as the most suitable. The candidates considered in this study were the silver-zinc battery, lithium thionyl chloride battery, sodium-sulfur battery, and fuel cells. Other likely future candidates were discussed briefly, but were not considered in the overall assessment because of their obvious need for further development.

#### 7.2 CONCLUSIONS

All the salient points, quantitative and qualitative, of the energy systems discussed in the previous chapters are summarized in Table 7-1. The sodium-sulfur batteries, because of their molten electrodes and the fact that they were so early on in their development, were considered to be, at the present time, the least acceptable of all energy systems covered. The lithium thionyl chloride battery had the highest energy density of all four systems. Despite early safety setbacks and development uncertainties, the lithium thionyl chloride battery shows promise of overcoming the obstacles in these areas in the future.



TABLE 7-1

## ENERGY SYSTEM SUMMARY

	YARDNEY LR-190 Ag-Zn	ALTUS HEDB LiSOCl <sub>2</sub>	Fuel Cells H <sub>2</sub> -O <sub>2</sub> (a) <sup>2</sup>	Alkaline (b)	Na-S
W-hr/lb	63	226.7	68	363	90
W-hr/in <sup>3</sup>	2.7	12.9	2.5	4-13 <sup>(c)</sup>	4
kW-hr:					
17 inch	31.2	149.6	29 <sup>(d)</sup>	46-151 <sup>(d)</sup>	46 <sup>(d)</sup>
25 inch <sup>(d)</sup>	118	375	63	100-325	100
Shelf life (yrs)	5	10	UNK	UNK	UNK
Operating safety	Very Good	Fair	Good	Good	Fair
Development time (years)	0	5-15	(e)	(e)	2

NOTES: (a) High pressure storage  
 (b) Cryogenic storage  
 (c) Uncertainty involves whether literature figure  
      includes entire system, or just fuel cell  
 (d) Projected capacity  
 (e) Depends on industry cooperation



The fuel cell's energy density suffered from the fact that all products and reactants were required to be stored on board. This requirement stemmed from the ballasting requirements for an undersea vehicle. In addition, off-the-shelf fuel cells were virtually non-existent, and there was no evidence of large scale development in the near future.

Of those energy systems covered, the silver-zinc battery was the most suitable for the low energy vehicle application described in Chapter 1. In addition to having more than enough energy storage capacity to meet the 16 kW-hr requirement, the silver-zinc battery's performance record was long and proven, and it was readily available in a wide variety of models. Of the remaining energy systems, the lithium thionyl chloride battery shows the most promise in the future of meeting the longer duration mission requirements.

### 7.3 RECOMMENDATIONS

The difficulties of thermal management associated with the molten electrodes of the sodium-sulfur secondary battery, combined with the uncertainties of the long term effects of freeze/thaw cycles on those electrodes, are major problems surrounding the application of this technology to an undersea vehicle. Further development of this energy system, therefore, is not recommended for this application, until this battery has been used successfully in other transportation situations.



Fuel cells require further study in the area of reactant storage, as well as development of a fuel cell of the proper size and energy requirements for undersea vehicle application. With regard to development for undersea applications, however, industry is unwilling to commit the research dollars without a guaranteed production rate, while actual application to undersea vehicles is unlikely without research. Unless this vicious cycle can be broken, the fuel cell seems destined to fall by the wayside in future undersea autonomous vehicle applications.

The lithium thionyl chloride battery was deemed the most promising for future applications, and with good reason. As discussed in Chapter 3, all of the battery's shortcomings are well documented, and industry has the steps in place to correct them over the course of the next five years. A detailed comparison between the lithium thionyl chloride battery and the lithium sulfurhexafluoride combustor systems will be required before a decision can be made on which is most suitable for longer duration vehicles, however.



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APPENDIX A

DESCRIPTION OF A TYPICAL SILVER-ZINC

DEEP SEA BATTERY

(An excerpt from Yardney Corporation's "Deep Submersible,  
High Energy, Silver-Zinc Batteries")



In current deep submergence technology, the battery is contained within a leak-proof box, the void spaces of which are filled with a non-reactive, di-electric compensating oil. Pressure is transmitted through a flexible member connected to the submersible's compensating system. The increase in pressure as the vehicle descends causes volume changes within the battery. The changes are due primarily to a decrease in volume in the gas held in and around the porous electrodes. The gas is slowly forced from the electrodes as pressure increases, while most of the electrolyte is absorbed by the separator and electrodes. The upper portion of each cell is also filled with compensating oil. As hydrostatic pressure increases in the system, additional oil enters the box from the compensator and flows into the cells to compensate for the reduced gas volume and any other pressure-induced volume changes. Among the latter are the compressibility of the potassium hydroxide electrolyte, approximately 2%, and that of the mineral oil of 5 to 7% between 0 and 15,000 psi.

To prevent oil from getting on or between the plates in the cell and reducing their effective working area, the oil floats atop a layer of electrolyte which at atmospheric pressure stands at some distance above the plate's tops. The cell's design must anticipate the maximum tilt angles so that the oil will not mask the plates, nor electrolyte spill from the vent. Separator height must also be extended since zinc tends to bridge over the separator (called zinc dendrites) if silver-zinc cells are charged for extended periods with



electrolyte higher than the separator. The electrolyte-oil interface, then, remains always below the separator top at atmospheric pressure and always above the electrode top at the maximum pressure and anticipated tilt angles.

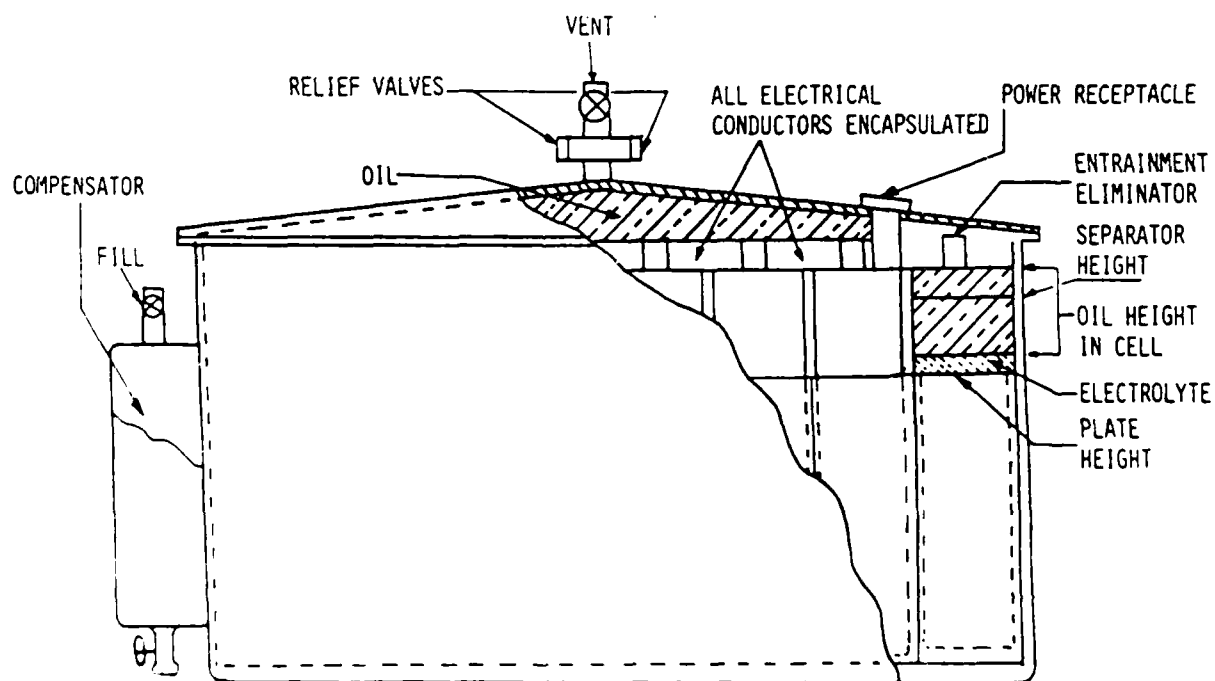
Pressure is equalized without and within the battery box by means of a diaphragm, bellows or bag. Yardney has found the latter to be most versatile. This compensator may be mounted either in the battery box or outside. In the first instance it opens only through the box wall to the sea. The battery is completely filled with oil before being sealed up and immersed. This collapses the compensator. When the vehicle descends into the sea, pressure outside the battery increases and water enters the compensator. The compensator can also be a separate component attached to, and opening into, the battery box. In this case, both box and compensator are filled with oil at atmospheric pressure, the oil moving from the compensator to the box as required to equalize the pressure. A layout of a typical silver-zinc deep ocean battery is shown in Figure A.1.

One problem arising with deep ocean cells not encountered in the same magnitude in other applications is electrolyte carry over or entrainment. Every bubble of gas carries a sizable film of electrolyte. In most applications this bubble loses its electrolyte at the electrolyte-air interface. In deep sea cells, however, it tends to continue through the oil and out of the cell. This leaves a conductive, corrosive film on the tops of the cells, the



hardware and in the box. Several different materials and configurations were tested for their effectiveness as de-entrainment devices. One of the best is a nylon net in a container sealed to the vent of each cell. By treating the net with an indicator before installation, it is possible to tell at a glance if electrolyte has been carried over.

Some gas will accumulate in the top of the battery box and may require venting during the final stage of ascent. To accomplish this, a relief valve that operates at approximately 1 psi is installed at the highest point in the battery box, the cover sloping toward that point from all directions.



Typical Deep Submergence Silver-Zinc Battery

Figure A.1



## APPENDIX B

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